ELEMENTS
AND
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BY

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INTRODUCTORY

DURING the last fifteen years, owing to the discoveries of Henri Becquerel, the Curies, Sir J. J. Thomson and his pupils, especially H. R. C. Wilson, Rutherford, Soddy, Perrin, and others, the ancient doctrine of the discrete nature of matter and the hypotheses of the existence of atoms and molecules have received new confirmation. Johnstone Stoney's "atom of electricity," the electron, has been shown to be separable from matter, and to be capable, under certain circumstances, of independent existence. It has also been made evident that the electron must be regarded as a kind of "element," with much stronger claims to "elementary," that is undecomposable, characters than the bodies hitherto ranked as "elements." It is with the object of presenting a consistent sketch of the progress of theory in this field that this book has been written.
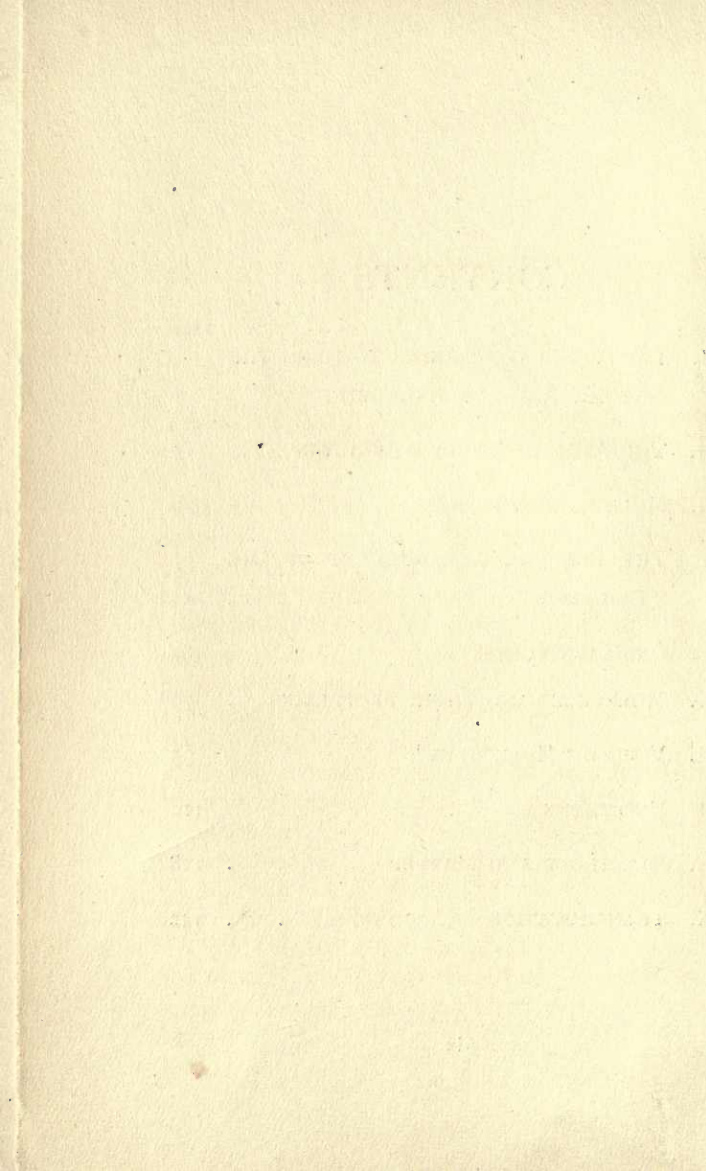
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ELEMENTS AND ELECTRONS

CHAPTER I

TWO VIEWS CONCERNING NATURE, THE ATOMIC AND THE ENERGETIC

AMONG the ancients, the first to foreshadow by his teaching the attitude of modern science towards Nature was Epicurus. Born in 341 B.C., seven years after the death of Plato, and almost twenty years before the death of Aristotle, he was in daily contact with men in Athens who had absorbed the teachings of these philosophers; and the founder of the sect of the Stoics, Zeno, was his contemporary. During his whole life, until his death at the age of seventy-one, Epicurus, like other philosophers of his age, gathered round him many of the youth of Athens; and by his example and precepts, he inculcated in them the teachings of his philosophy. With much of this we have no concern here; it is necessary, however, to consider one of his principles—a fundamental one for his views of Nature and existence; and also to touch on one of his doctrines which more nearly concerns

the subject of this book—his conception of atoms and the part they play in the physical universe.

The Epicureans appealed to the senses as the final criterion ; not necessarily the unaided senses, but the senses reinforced by all useful adjuncts. They allowed, however, that the deductions from sense-impressions might be erroneous, and that one should be on one's guard against drawing wrong conclusions. They also postulated that it is possible to draw from sense-impressions deductions as regards the structure of bodies which cannot be verified by the unaided senses ; such, for example, as that matter has an atomic structure ; but a fundamental tenet of their philosophy was, that in picturing minute structure and occurrences to our minds, we must argue from the known to the unknown, from the great to the small, from the tangible to the intangible. Everything is constructed on the same, or approximately the same, pattern as what we can observe by sight and touch ; Nature is to be explained by the two conceptions of matter and its motion. The word " explain " can only be interpreted in this fashion ; unless we can picture the minute operations of Nature as analogous to those which we can investigate by our aided or unaided senses, these operations are not " made clear."

Now, this is the attitude of mind of the modern man of science. He endeavours to picture the chemical and physical changes which take place

in almost every object which comes under his observation as similar in character to those which affect his senses ; he regards the molecular as analogous to, and as comparable with, the " molar " ; he endeavours to construct, either actually or mentally, machines which will fulfil certain functions, and produce certain changes like those which are found to occur when matter modifies its physical and chemical properties. It is this method which, although in some respects inconsistent with certain beliefs, has led to the great advance in physical science, so marked in our age. It is true that the Epicureans did not forestall the moderns in their appeal to experiment ; had they done so, the birth of science would have taken place in their era. But they strongly insisted on the necessity of accurate definition ; each word, each expression employed, must correspond with a definite reality. The conceptions attached to language must not be hazy and elusive ; each conception, too, must be the outcome of some definite perception. These conceptions were to be made subject to reasoning ; it was held to be possible to deduce conclusions not necessarily evident from a first glance at the facts. But the age was not ripe for this method, since adopted with so much success. Like other contemporaneous systems of philosophy, Epicureanism concerned itself more with man's life and conduct than with the investigation of natural

objects and occurrences ; it put aside the phenomena of Nature as not of direct service in helping mankind to live well. For this reason, no progress in physical science was made. But, like the moderns, the Epicureans regarded the ultimate revelation of the senses as dealing with matter and its motion. Matter alone is real ; motion the form in which the existence of matter manifests itself. What is not matter does not exist. And matter is " that which can be touched." Touch is impact on the organs of sense ; and impact is due to a body in motion.

But what is a body ? Matter, according to the Epicureans, is indestructible ; and " body " is the capacity of acting, or being acted on, presumably by another " body." The nature of " body " as such, apart from the attributes (a question which greatly occupied the Schoolmen at a much later period of the world's history), had already been considered by Leucippus and Democritus (430 B.C.). The secondary attributes or properties, such as weight, colour, shape, etc., were distinguished from the primary attributes, which were regarded as having no concern with human observation, but nevertheless essential to the existence of matter. Democritus regarded matter or body as what fills space ; when absent, space is empty. There he stopped ; it was regarded as useless to enquire further into the real nature of body or matter ; and attention was limited to its

structure. This, it was believed, consisted in atoms ; indivisible portions. But not all atoms, according to the notions of Democritus, are alike ; they differ in shape, order, and position, and probably in size and in weight. It would appear, however, that Democritus regarded weight not as a property of any individual atom, but only of collections of atoms ; although this point is obscure, and may mean merely that individual atoms are invisible, and that only aggregates can be seen. The atom is not a mathematical point ; it has extension, it is also solid and impenetrable ; and because indivisible, it is also indestructible. Yet collections of atoms can be destroyed ; they can rearrange themselves into other groupings. It is these groupings which form natural objects— the sun and stars, all earthly objects, animate and inanimate ; all consist of groupings of atoms. Even the soul and mind consist of atoms, but more " subtle " ; of a smaller size, and a more smooth and regular form.

These ideas were adopted by Epicurus from Democritus. But Democritus held that when the atoms move, they form vortices and revolve, imagining that the heavier atom, when moving, would overtake the lighter ; he was misled, no doubt, by the fact that when objects fall through the air, light bodies fall more slowly than heavy ones ; this would, he believed, give rise to circular motion.

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We need not follow Epicurus into his curious view that the atoms fall downwards through space in parallel lines. These views are fully stated by Lucretius in his poem " De Rerum Natura " (about 90 B.C. ; the 171st Olympiad). But in free space there is no " upwards " and " downwards " ; this point of view was not touched. The question was : " How do the atoms aggregate into matter ? How do they arrange themselves, if they fall in parallel lines ? " In modern phraseology, they were regarded as possessing the rudiments of choice, of free-will. Owing to this, the atoms left their rectilinear paths and grouped themselves : and of. these groupings all that we know is made.

During the Middle Ages the tendency was to argue without any reference to experimental proof. It was, indeed, only in isolated cases that experiment was resorted to. The alchemists, in their search for the " philosopher's stone " and for the " elixir vitæ," the former the means of changing the baser metals into gold, the latter the means of conferring perpetual youth on its fortunate possessor, made experiments of a kind ; but they were made with no real knowledge of what was attempted, and generally at random ; Nature was not interrogated. The question as to the nature of matter was left to scholastics ; and discussions were common as to whether matter should be regarded as a *plenum*, a *continuum*, that is, whether

space inhabited by matter is completely filled ; or, on the other hand, whether matter should be regarded as made up of small particles, with interstices between them. In a *continuum*, matter must be capable of infinite subdivision. It is, of course, mentally inconceivable that an object can be divided into parts so small that one of the parts cannot be further divided ; such a conception negatives the possibility of the infinitesimal ; and our minds are so constituted that it is as impossible to conceive of an inferior limit to space, as of a superior limit. We cannot think of anything so small that it cannot be mentally halved, or of anything so great that it cannot be doubled. From this point of view, matter must be regarded as infinitely divisible, and therefore all objects must have a continuous nature. Indeed, our unaided senses force us to this conclusion. For it is impossible to detect any grained structure in water or in jelly ; and though a material like sandstone does show a grained structure, each particle of which it is composed, identical with rock-crystal, appears to be as uniform or homogeneous as ice.

The other view, that matter consists of atoms or small particles, advanced by Empedocles and adopted by the Epicurean school of philosophers, apparently contradicts the doctrine of the continuity of matter. According to it, although atoms may be regarded as capable of division by an

effort of thought, yet they are not divisible in reality; or perhaps it would be better to say that it is unnecessary to conceive of their divisibility, such a conception serving no useful purpose.

There is, however, another method of regarding phenomena (and by phenomena is meant whatever directly or indirectly impresses our senses and becomes a subject of thought) which rests on a different foundation. It has been supported chiefly by Wilhelm Ostwald, late Professor of Physical Chemistry at Leipzig, and by his school ; but it is not generally adopted by physicists and chemists, even although it affords a consistent explanation of phenomena, and, indeed, it is understood that its author has abandoned it.

The term " Energy," used in a physical sense, was first introduced by Sir William Thomson, later Lord Kelvin, and Macquorne Rankine, Professor of Engineering in Glasgow, about the middle of last century. Energy may be defined as a capacity for doing work. When we coil a spring, we store energy ; for work may be done by the spring in uncoiling itself, as when a watch goes. When we raise the weight of a clock, we store energy, for its fall actuates the works. If we enquire into the cause of motion of a bullet fired from a gun, which also does work, we must attribute it to the energy contained in the powder. The work done by a steam-engine is primarily due

to the expansion of the steam from a small to a large volume in the cylinder ; compressed steam, therefore, contains available energy. If we ask further whence the steam acquires its energy, we must attribute it to the fuel, which in burning develops heat ; the energy must therefore reside in the coal, and in the oxygen of the air, which, when they combine, give heat. Energy is thus whatever can be converted into work.

But what is work ? Although this word is used loosely, it may be defined as the raising of a weight against the attraction of the earth. If, in the English system of units, a mass weighing a pound be raised through one foot, one foot-pound of work has been done. Twice that amount of work is done if the pound be raised through two feet, or if two pounds be raised through one foot. This, of course, implies that the earth exerts a constant pull on the mass which we agree to call one pound, and that is not the case. For the pull exerted by the earth varies, according to the position of the mass on its surface. Because the earth is not a sphere, but is flattened at the poles, and because the attraction of the earth on any object is greater the nearer that object to its centre, a thing has a somewhat greater weight as it approaches the pole. Again, the earth is revolving at a great speed on its axis ; and this motion tends to throw an object on its surface into space. At the poles, of course, there is no such tendency ; at the

equator, it is at its maximum. Hence a second reason why an object weighs less at the equator than at the poles.

In defining work, then, account has to be taken of the position of the object on the earth's surface. Sometimes the latitude of Greenwich is fixed on for this measurement; sometimes latitude 45°; but it is easy to compare units of work by multiplying them by a factor termed g, which varies with the latitude, and which makes allowance for such changes in position.

Besides being measured by raising a weight from the earth's surface, work may also be measured by setting a mass in motion. It obviously requires very different efforts to set in motion a bicycle and a locomotive; to fire a bullet from a pistol, and to propel a shot from a cannon. Suppose the propulsion of a piece of matter—a mass—were caused by a spring, the work done by the spring would depend on the magnitude of the mass; a mass double the magnitude would require twice as much work to make it move at a given rate. Suppose it requires a certain amount of work, which we shall call W, to make a mass M move at a velocity or rate C. If M is increased to 2M, then the work is doubled. Now, rate, or velocity, is distance traversed by a moving object in unit time; for instance, miles per hour, or feet per second. If C stands as a symbol for celerity or velocity, L for length or distance, and

T for time in seconds, $C=L/T$; velocity is equal to length per unit time. Now, suppose a mass moving with uniform velocity; and that that velocity is increased uniformly, or uniformly accelerated; the velocity changes, or increases by a definite amount for each unit of time, say each second; hence we have as the result C/T, or $L/T \times T$. This expression denotes acceleration. To accelerate the rate of motion of a mass requires a force to be continuously applied, hence the force $= M \times L/T \times T$, or ML/T^2. Let us next suppose that the mass starts from rest, and that the force acts for one second; and that at the end of the second the velocity is unity. The mean between no motion, o, and unit motion, I, is $\frac{1}{2}$. Hence by this arbitrary choice of a unit, the unit of force, which we may call $F = \frac{1}{2}ML/T^2$. Reverting again to our original unit of work, raising a weight, a mass has to be raised against gravitational force through a definite distance, or in symbols, Energy, $E = F \times L$. Now if $F = \frac{1}{2}ML/T^2$, E must equal $(\frac{1}{2}ML/T^2) \times L$ or $\frac{1}{2}ML^2/T^2$. But L^2/T^2 is the same as C^2; and thus we get for the equation, Energy, $E = \frac{1}{2}MC^2$.

This one form of energy differs from the other in kind; it is the energy of a mass in motion. The former is the energy of a force overcoming an attraction. By choosing suitable units, we may have the energy of work of both kinds equal; we might in fact use the energy of a mass in motion for the purpose of raising a weight, or we might

use the falling of a weight as a means of setting a mass in motion. Hence

$$M = \frac{E}{\frac{1}{2}L^2/T^2} = \frac{2E}{C^2}.$$

The first of these kinds of energy may be termed gravitational energy, or, more generally, *linear* energy, for, as a rule, it is exerted in a straight line ; the second is named *kinetic* energy, from the Greek word *kinesis*, motion. Both have as their fundamental units length, time, and mass. If these are all known numerically, a numerical value can be given to energy. If the gram be chosen as unit of mass, the second as unit of time, and the centimetre as unit of length, we have what is termed the CGS system ; and the unit of energy is named an *erg*. From this can be deduced the unit of force ; it is the force which, when applied to a mass of one gram, will cause it to accelerate its rate of motion one centimetre per second ; it is named a *dyne*. A gram weight presses on the earth with a force of about 981 dynes at Greenwich. This is the force of the earth's attraction, or ' g.'

This detailed explanation has been necessary, because the conceptions involved are essential to an understanding of the theory of Ostwald, as well as of much of the contents of this book. There are here four fundamental ideas—energy, mass, time, and space. If any three of them are known, the fourth can be deduced by the rule of three. Now,

from the beginning of the world, the three funda-
mentals chosen have been mass, time, and space or
distance ; and energy, a modern conception, has
been derived from these. But it is equally possible
to assume any other three of the four conceptions
as fundamental, and to deduce the fourth. Ostwald
proposed to assume energy as a fundamental
concept, or, as the Germans would say, a " Ding
an sich," a thing by itself, instead of mass ; in
that case mass, $M = 2E/C^2$.

The word mass has two meanings. The original
one was, no doubt, a lump, or quantity of matter,
and in this sense it is practically synonymous with
the word matter. But as a lump of matter can
be measured by its resistance to being moved,
commonly termed *inertia*, and as the greater the
quantity of matter the greater the difficulty of
moving it, or the greater its inertia, great mass was
associated with great inertia, and the word mass
grew to signify " the measure of a quantity of
matter." The M in the foregoing equations has the
latter meaning ; it is the measure of a quantity of
matter. But why " of matter " ? It may be re-
garded as a physical entity, practically identical
with inertia, or resistance to being moved. Now,
Ostwald and his school suggest that the letter M
in these equations is merely a physical quantity,
and that to suppose the existence of a substratum
which we call " matter " is unnecessary and
superfluous. Mass, in fine, is defined as the

quotient, energy divided by $\frac{1}{2}C^2$. And this Ostwald defends on the ground, among others, that all that we know through the senses is the result of changes in our energy content; and that we have no more right to deduce from these changes the existence of a substratum of matter than had the Schoolmen a right to conclude that some substratum common to all things underlay their properties, such as form, colour, resistance to touch, and so on.

We see, therefore, that there are two possible views of Nature, the first that such a substratum exists; the second that there is no such substratum, but that all that we know is derived from our conceptions of time, space, and energy. There are also two possible variations of the first view: that matter is continuous, and not composed of particles; and, on the other hand, that it is discrete and composed of particles or atoms. The older view, that there is a substratum, matter, and that its structure is a grained one, is now almost universally held to be true; but it should be noted that the energetic representation of Nature is self-consistent, although it may not lend itself to a pictorial representation of phenomena, and does not appear to suggest fresh experiments so well as the material representation of Nature does. It is well to remember, nevertheless, that thought cannot place a limit on the size of the particles of which matter is supposed to consist; and that in

strict logic these particles themselves must be held to possess a structure. We shall see in the chapters which follow, that the modern tendency is to conceive of an order of particles smaller than the atom, of which the atom is built up ; but at present, questions regarding the structure of these smaller particles, which have been termed electrons, are generally ignored.

CHAPTER II

THE ATOMIC THEORY OF DALTON

WE have seen in the preceding chapter that the ancient doctrine that matter is discrete, held by the Greek philosophers, was expounded by Lucretius in his celebrated poem "De Rerum Natura." It led to no progress, however, for it did not induce the experimental investigation of Nature ; and it was not till the beginning of last century that it received a practical application from the fertile brain of Dalton. In investigating the cause of the pressure of the atmosphere, he recognized that each constituent gas exerts its own pressure, as if the other gases were wholly absent. The expression of his law was : " One gas behaves to another as if it were a vacuum." For example, taking the atmosphere as consisting of 1 part by volume of oxygen and 4 parts of nitrogen (and this nearly expresses its composition), and assuming the total pressure as equal to that of a column of mercury 30 inches in length (the normal height of a barometer), the pressure of the oxygen is $\frac{1}{5}$th of 30, or 6 inches, and that of the nitrogen $\frac{4}{5}$ths of 30, or 24 inches, the sum of the two being the total pressure, equal to

30 inches. To explain this fact, he supposed the pressure of each gas to be due to the small particles or atoms of which it consists ; and from this he was led to consider whether the relative weights of the particles or atoms could be determined. He went on the supposition that chemical compounds, such as water, consist of simple numbers of atoms in juxtaposition ; and it followed that the relative weights of the atoms could be determined, if one knew the relative numbers in the compound, and if the weight of one particular kind were made the standard. He then collected analyses which had already been made, and supplemented them by others of his own ; but in what follows we shall adopt more accurate numbers, for Dalton was a poor analyst.

" In all chemical investigations," Dalton wrote, " it has justly been considered an important object to ascertain the relative weights of the simples which constitute a compound. But unfortunately the inquiry has terminated here ; whereas from the relative weights in the mass, the relative weights of the ultimate particles or atoms might have been inferred, from which their number and weights in various other compounds would appear, in order to assist and to guide future investigation, and to correct their results. Now it is one great object of this work [*A New System of Chemical Philosophy*, 1808] to show the importance and advantage of ascertaining the relative weights of

the ultimate particles both of simple and compound bodies, the number of simple and elementary particles which constitute one compound particle and the number of less compound particles which enter into the formation of one more compound particle." Thus, if one particle of water consists of two smaller particles, one being hydrogen and the other oxygen, then as one part of the former by weight combines with 8 parts of the latter, their respective atomic weights are as 1 : 8.

But Dalton was mistaken in laying down arbitrary rules, supposed to indicate the number of atoms present in the compound particle, or as we now term it, " molecule." His rules were :—

1 atom A+1 atom B=1 atom C=a binary particle.
1 „ A+2 „ B=1 „ D=a ternary   „
2 „ A+1 „ B=1 „ E=a   „   „
1 „ A+3 „ B=1 „ F=a quaternary „
3 „ A+1 „ B=1 „ G=a   „   „

" When one compound can be obtained only, it must be presumed to be binary ; when two, they must be presumed to be binary and ternary. When three, one we expect to be binary, and two ternary. When four combinations are observed, we should expect one binary, two ternary, and one quaternary, etc." " From the application of these rules to the chemical facts already ascertained, we deduce the following conclusions : First, water is a binary compound of hydrogen and oxygen, and

the relative weights of the two elementary atoms are as $1 : 7$ (really $1 : 8$) nearly. Second, that ammonia is a binary compound of hydrogen and azote, and that the relative weights of the two atoms are as $1 : 5$ nearly (really $1 : 4·66$). In all these cases, the weights are expressed in atoms of hydrogen, each of which is denoted by unity."

The arbitrariness of these so-called rules was pointed out at the time ; nevertheless, one of Dalton's main ideas is still our chief guide to exact determinations of atomic weights in all ordinary cases. It is : " From the relative weights in the mass (of the compound), the relative weights of the ultimate particles of the bodies, or atoms (i.e. of the constituents) might have been inferred." This we now express by saying that the atomic weight of an element is an exact multiple of its equivalent.

Dalton, as we have seen, fixed on hydrogen as the standard of atomic weights, and for some time his example was followed, although hydrogen forms relatively few compounds, so that but few direct ratios can be observed. On the other hand, oxygen combines with most elements, so that many ratios between the weights of elements and the weights of oxygen in their oxides can be directly determined ; hence Berzelius referred atomic weights to oxygen, taken as 100. At present, the International Commission of Atomic Weights have accepted as the standard of comparison oxygen$=16$; the ratio $16 : 15·88$, or

1·008 : 1 reduces the present atomic weights to the hydrogen standard.

The expression equivalent has been used; it can be defined on either standard as (A) the weight of an element combining with or displacing 1 part by weight of hydrogen or 7·94 parts of oxygen; or (B) the weight of an element combining with or displacing 8 parts of oxygen or 1·008 parts of hydrogen.

The atomic weight of an element is always some exact multiple of the equivalent, thus : Suppose the equivalent of an element to have been found to equal 9 ; that is, suppose that analysis has proved that 9 parts by weight of the element combine with 1·008 part of hydrogen, or with 16 parts of oxygen, then the element will have an atomic weight depending on the factor with which the equivalent is multiplied, thus :—

$$\text{Equivalent of an element} = 9.$$

Equivalent × *factor* termed the *valency* = *Atomic weight*. Formula of oxide

9	×	1	= 9	E_2O
9	×	2	= 18	$E\,O$
9	×	3	= 27	E_2O_3
9	×	4	= 36	$E\,O_2$
9	×	5	= 45	E_2O_5

How can that factor be determined ? There are several methods, which we will next consider.

In 1802, Dalton published six papers in the *Memoirs of the Literary and Scientific Society of Manchester*, in the last of which, according to Thomson, Dalton showed " that all elastic fluids

expand the same quantity by the same addition of heat, and this expansion is 1/480th part for every degree of Fahrenheit's thermometer." The equivalent for this figure in centigrade degrees is 1/267th. Three years later, Gay-Lussac, incited by Humboldt, announced that 2 volumes of hydrogen combine with 1 volume of oxygen, if the volumes of these gases are compared under identical conditions of temperature and pressure; and he found that the expansion of a gas amounts to 1/273rd of its volume at 0°C, if pressure be kept constant. Gay-Lussac's name is usually associated with this law; as is that of Robert Boyle with the law that, at constant temperature, the volume of a gas varies inversely as the pressure to which it is exposed.

Continuing his investigations, Gay-Lussac, in 1808, published the further discovery, that other gases combine in simple volumetric proportions, and that the compounds produced, if gaseous, have volumes bearing simple numerical relations to those of the combining gases. Thus he found that :—

2 volumes carbonic oxide+1 volume oxygen
    =2 volumes carbon dioxide ;
2 volumes nitrogen+1 volume oxygen
    =2 volumes nitrous oxide ;
1 volume nitric oxide+1 volume oxygen
    =2 volumes nitric peroxide ;
3 volumes hydrogen+1 volume nitrogen
    =2 volumes ammonia.

And he further observed that the weights of these volumes bore simple relationships to the combining weights of the several gases, and eventually came to the conclusion that the weights of equal volumes of gases at the same temperature and pressure are proportional to their atomic weights ; or if hydrogen be taken as unity, both as regards the atomic weights and the specific gravities of gases, that the latter are identical with their atomic weights.

It has been stated that Dalton had also thought of this law, previous to its announcement by Gay-Lussac, and that he came to the conclusion that it was erroneous, because 1 volume of nitrogen (x atoms) plus 1 volume of oxygen (x atoms) give 2 volumes of nitric oxide (2x atoms), instead of 1 volume=1 atom (or molecule, as we now term it).

Now, putting together Dalton's idea that compounds consist of definite numbers of atoms, with Gay-Lussac's discovery that the volumes of compound gases bear a simple relation to the volumes of the component gases, it is evident that some simple theory should form a bond of connection between them.

Take the case of water. The facts are that water has the invariable composition :—

|		By weight.		By volume.
Oxygen	.	8 parts	...	1 part.
Hydrogen	.	1 part	...	2 parts.

But 9 parts of gaseous water do not occupy 3 volumes, as one might at first expect, but almost exactly 2 volumes. How is this to be accounted for ? If the volume of the water-gas had been 3, it might have been stated : " Equal volumes of gases contain equal numbers of atoms." But as the volume of the water-gas is 2, and not 3, that statement cannot hold, for 2 volumes of water-gas would then contain the same number of atoms as the 3 volumes of mixed hydrogen and oxygen before combination.

This riddle was solved by Amedeo Avogadro in 1813. His solution was as follows : Matter is not so simple as Dalton supposed. When hydrogen and oxygen unite, supposing we assign to an atom of hydrogen the symbol H, and to an atom of oxygen the symbol O, then combination is not represented by the equation

$$2H + O = H^2O,$$
$$\text{2 vols.} \quad \text{1 vol.} \quad \text{2 vols.,}$$
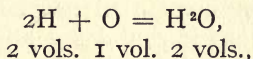
for then 3 volumes of the mixed gases would contain as many atoms as 2 volumes of gaseous water ; but by the equation

$$2H^2 + O^2 = 2H^2O,$$
$$\text{2 vols.} \quad \text{1 vol.} \quad \text{2 vols.,}$$
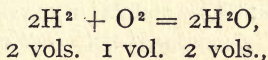
and it must be recognized that the unit of hydrogen, as well as the unit of oxygen *in the free state*, i.e. as gases, is not the atom, but the molecule

(diminutive of *moles,* a heap). The law connecting the atomic weights with the volumes of gases is therefore not "equal volumes of gases contain equal numbers of atoms," for that is manifestly false, but "equal volumes of gases contain equal numbers of molecules." Hence, as we see, two molecules of hydrogen plus one molecule of oxygen yield two molecules of water-vapour ; and the two molecules of water-vapour inhabit the same volume as the two molecules of hydrogen which go to form it.

Water-gas, compared with hydrogen at the same temperature and pressure, is found to be 9 times as heavy ; that is, a molecule of water-gas is 9 times as heavy as a molecule of hydrogen. How many times is it heavier than an atom of hydrogen ? It is evident that a molecule of hydrogen must contain at least 2 atoms, if Avogadro's Law is to hold. It might contain a larger number ; but the supposition that it contains 2 atoms will satisfy the law ; and there are further reasons for supposing that this supposition is correct. A molecule of water-gas is thus 18 times heavier than an atom of hydrogen ; and this statement can be made general : *The molecular weight of a gas is twice its density compared with that of hydrogen, at the same temperature and pressure.* From this relation, the atomic weight of the elements contained in gaseous compounds may often be found. Thus, a compound of sulphur with oxygen is known,

named sulphurous anhydride, which is composed of 32 parts of sulphur in combination with 32 parts of oxygen ; and it is 32 times as heavy as hydrogen. Its molecular weight is therefore 64 ; and this corresponds to a content of 2 atoms of oxygen, each weighing 16. That the atomic weight of sulphur is 32 cannot be inferred ; for the compound might contain more than one atom of sulphur.

Attention must now be directed to a discovery due to Dulong and Petit, Director and Professor at the École Polytechnique at Paris, a school for military engineers. To heat up the same weight of different substances requires very different amounts of heat. Here, a unit of heat is necessary ; and the one proposed, and still used, is termed a " calory " ; it is the heat which must be put into a gram of water in order to raise its temperature from 17° to 18° centigrade ; this is the same as the hundredth part of the heat required to raise the temperature of a gram of water from the freezing-point 0° to the boiling-point 100°C.

To heat 1 gram of sulphur through 1°C. requires only 0·194 calory ; to raise the temperature of 1 gram of lead from 18° to 19°, still less heat, 0·03 calory, is sufficient. Now, analysis has shown that a compound of sulphur and hydrogen, termed hydrogen sulphide, contains for every 1 part of hydrogen 16 parts of sulphur ; 16 is therefore the *equivalent* of sulphur. In lead sulphide, again, it

has been found by analysis that 103·5 parts by weight of lead are combined with 16 of sulphur ; 103·5 is therefore the equivalent of lead in that compound, for 103·5 parts of lead *replace* 1 part of hydrogen, and are equivalent to it.

The discovery made by Dulong and Petit in 1819 was this : Equal numbers of atoms of elements in the solid or liquid state require the same amount of heat approximately to raise their temperature equally ; or to express the same idea otherwise, the specific heats of elements (i.e. the amount of heat required to raise the temperature of 1 gram through 1°) are nearly inversely as their atomic weights. Hence the atomic weight of sulphur is to the atomic weight of lead as 0·03 is to 0·194. The same reasoning applies to the atomic weight of sulphur as was shown to hold for oxygen ; its atomic weight, 32, is twice its equivalent, 16, just as that of oxygen is twice 8, its equivalent. Hence as 0·03 : 0·194 : : 32 : 207 ; and 207 is therefore the atomic weight of lead. But the proportion in which sulphur and lead are present in galena (the sulphide) is 32 : 207 ; hence the formula is PbS, or Pb^2S^2, or Pb^3S^3 ; it contains equal numbers of atoms of each element. Does it contain one atom of each ? That we do not know, for we have no method for determining the molecular complexity of solids.

The density in the state of gas, or the " vapour-density " of sulphur, has been determined. How

does it fit the theory? The facts are: At the boiling-point of sulphur at atmospheric pressure, 444·5°, and at lower temperatures (for it is possible to make sulphur boil at a lower temperature by lowering the pressure), the density of sulphur vapour approximates to $128 = 4 \times 32$. As the temperature rises, the density compared with hydrogen at the same temperature and pressure gradually falls, until at very high temperatures— 1000° and above—the density of sulphur vapour is 32, and that is the same as its atomic weight, deduced from determination of its specific heat. It will be remembered that the molecular formula of hydrogen is H_2, and that of oxygen, O_2; their densities being 1 : 16, that is, a molecule of oxygen is 16 times as heavy as a molecule of hydrogen, for equal numbers of molecules inhabit the same volume; but as in this case, each molecule of hydrogen or of oxygen of two atoms, it follows that an atom of oxygen is 16 times as heavy as an atom of hydrogen. The same reasoning is applied to sulphur vapour; at high temperatures, it is believed that each molecule of sulphur consists of two atoms; a molecule of sulphur vapour is thus 32 times as heavy as a molecule of hydrogen, and consequently the weight of an atom of sulphur, or its atomic weight, is 32 times as great as that of an atom of hydrogen.

How is the greater density of sulphur vapour at low temperatures to be accounted for? The

number 128 implies that the sulphur molecule is 128 times as heavy as the hydrogen molecule, and if the hydrogen molecule consists of 2 atoms, then the sulphur molecule is 254 times as heavy as the hydrogen atom. But $254 = 8 \times 32$; it is therefore concluded that there are 8 atoms in a sulphur molecule at low temperatures ; the formula of sulphur is thus S^8. It may be asked, is the formula not S^6 or perhaps S^4 at intermediate temperatures ? No ; for if it were, there would be a region of comparative stability at temperatures where such molecules might be supposed to exist ; there is, however, no sign of such stability ; the density of sulphur vapour falls continuously with rise of temperature, and there are no halting-places where density remains constant or approximately constant over a range of temperature, the existence of which might lead to the supposition that less complicated molecular groupings between S^8 and S^2 are capable of existence.

To phenomena of this kind—the gradual simplification of the molecule with rise of temperature, and its re-complication with fall of temperature—the name " dissociation " was given in 1866 by Saint-Claire Deville, a well-known French chemist of last century.

CHAPTER III

MOLECULAR WEIGHTS

FROM Avogadro's Law, that equal volumes of gases at the same temperature and pressure contain the same number of molecules, it is possible to deduce the molecular weight of any compound which can be obtained in the state of gas. For it is very certain that a molecule of oxygen consists of two atoms ; and by taking the density of oxygen as 16, and comparing the density of any other gas on this standard, the molecular weight of that gas can be ascertained by doubling the figure obtained for the density.

Certain substances, however, like sulphur, mentioned in last chapter, have more complicated molecules at low than at high temperatures. Another case is iodine, of which the atomic weight, deduced from the specific heat, and from the equivalent, is 127. At moderate temperatures, say 500°C., its vapour-density is also 127 ; and from this it is concluded that its molecule, like those of oxygen and hydrogen, consists of two atoms. Victor Meyer, late Professor at Heidelberg, discovered that at 1700°, under low pressure,

the density is reduced to 63·5, half of 127 ; that can be interpreted only on the supposition that the molecules of I^2 dissociate into molecules of I^1 at that very high temperature ; as the temperature falls, re-combination occurs, and the molecule I^2 is reproduced by union of molecules, or what is here the same, of atoms of I^1.

Sulphur and iodine are both " elements," or rather compounds of one atom with another, or with more than one other atom of the same kind. But instances of dissociation of compounds are not infrequent, where the products of dissociation differ from one another. Ammonium chloride is an instance of such a compound. Its formula is NH^4Cl ; it is a white salt, not unlike common salt, with a saline taste ; it is made by mixing the colourless, transparent gases ammonia, NH^3, and hydrogen chloride, HCl. When heated to about 400° it becomes gaseous ; and for long it was supposed to yield ammonium chloride gas. But that gas would possess the same formula, NH^4Cl, and its molecular weight should be the sum of the atomic weights, viz. N,14+H,4+Cl,35·5, in all 53·5 ; its vapour-density should therefore be 53·5/2, or 26·75. By actual experiment, however, the density of the gas obtained from it was found to be 26·75/2, or 13·375. Multiplying the last number, as usual, by 2, to compare the molecular weight with that of an atom of hydrogen, the product, 26·75, is the mean molecular weight of

the gases into which ammonium chloride dissociates, viz. NH_3, of which the molecular weight is 17, and hydrogen chloride, of molecular weight 36·5 ; for $(17+36·5)/2=26·75$. It was discovered by Thomas Graham that light gases pass through a narrow opening more rapidly than heavy ones ; and this gave the way of actually determining by experiment that the gas from ammonium chloride is a mixture. Graham's Law is, that the rate of passage, or rate of diffusion of two gases, is inversely as the square roots of their densities ; one would expect, therefore, that for every 4 parts of hydrogen chloride passing (4 is nearly the square root of 17), 6 parts of ammonia should pass through (6 being nearly the square root of 36·5). This has been found by experiment to be the case.

We have seen that the weight of a molecule, relatively to the atomic weight of hydrogen, can be ascertained by taking the density of the element or compound in the state of gas ; but in the solid state, we have no such sure guide. Many solid substances, however, dissolve in water or in some other solvent such as alcohol, or oils of various kinds ; it is legitimate to ask whether the molecular weight of a dissolved substance can be ascertained. This has been found possible owing to the discoveries of Raoult, late Professor of Chemistry at Grenoble, and of Pfeffer, Professor of Botany at Leipzig. The reasoning, however, is

due to van't Hoff, late Professor of Physical Chemistry at Berlin ; his epoch-making paper was published in 1887, and of this a short account will now be given. The acceptance of these doctrines was greatly facilitated by W. Ostwald, late Professor of Physical Chemistry in Leipzig, in whose *Journal of Physical Chemistry* the first account of the theory appeared.

The ascent of sap in plants had long been a puzzle to botanists. Capillary attraction, or the rise of liquid in a narrow tube, had been suggested as a cause ; but this rise is entirely insufficient to account for the rise of sap to the top of a high tree. Pfeffer investigated another possible cause of rise : it might be due to what was termed " osmotic pressure " ; to the passage of water through a membrane, the cell-walls of the plant, into the cells ; for it was known that water enters the cells, rather than leaves them. Such walls are said to be " semi-permeable," for they are penetrable to water, but not to salts. The juice in the cells contains substances in solution, and water enters into such solutions. Pfeffer, in 1877, was successful in imitating the cell-walls of a plant by a device adopted by Traube in 1867, namely by impregnating a pot of porous earthenware with a slimy precipitate of a substance known as copper ferrocyanide ; alone, this slimy substance cannot withstand pressure, as may well be supposed ; but if made to adhere to the porous interior of a clay

pot, a vessel could be constructed through the walls of which water would pass in either direction. Pfeffer found, however, that if the water contained ordinary sugar in solution, the sugar would not penetrate these prepared walls, which were therefore termed " semi-permeable," that is, permeable to water, but not to sugar.

To measure the pressure of the entering water, the pot was filled with a dilute solution of sugar, and was closed with a stopper connected with a gauge for measuring pressure, and the pot was placed in a vessel containing water. Water entered and increased the pressure up to an amount proportional to the concentration of the sugar solution. Pfeffer also found that at a higher temperature the pressure produced by the entering solution was higher.

The word " concentration " has been used. What is its precise meaning ? A concentrated solution means a solution which contains much dissolved matter in proportion to its volume. If we dissolve an ounce of sugar in a quart of water, we have a solution of a certain concentration. If we dissolve two ounces of sugar in a quart of water, we have a solution of twice the concentration. Concentration may therefore be defined as weight of dissolved substance per unit volume of solution. The dissolved substance, in this case sugar, is spread through double the volume if it is dissolved in twice the volume of water.

It would be legitimate, also, to use the word "concentration" for the amount of a gas present in unit volume. Suppose that we had a quart bottle full of air at atmospheric pressure ; if another quart of air were pumped into the bottle, the "concentration" of the air would be doubled ; there would be twice as many molecules of oxygen and nitrogen in the same volume. And from Boyle's Law, we know that the pressure of that air would be doubled. If the temperature of the air were raised $1°$, and if the air were free to expand, it would increase its volume according to the scale of the absolute thermometer, of which the zero is $-273°C$. But if the air cannot expand, it will increase its pressure according to Gay-Lussac's Law.

Now, Pfeffer's discovery amounted to this : the osmotic pressure of a dissolved substance follows the same laws as the pressure of a gas ; it is proportional to the weight of substance present in unit volume, or, in other words, proportional to the number of molecules present, whether of dissolved substance, or of gas. Again, Pfeffer found that the pressure of a dissolved substance increases directly as absolute temperature rises ; this is the counterpart of Gay-Lussac's Law, applied to solutions.

But van't Hoff went further ; he showed that the osmotic pressure exerted by a known weight of sugar contained in a known volume of water was identical with the pressure which would have been reduced by a gas consisting of a number of

molecules equal to those of the sugar. The comparative weight of a molecule of sugar is 342 ; that is, a molecule of sugar is 342 times as heavy as an atom of hydrogen. Now, the osmotic pressure exerted by the sugar is such that 342 parts by weight of sugar in solution in a given volume exerts as much osmotic pressure as 2 parts by weight of hydrogen gas exerts, when made to occupy the same volume as the sugar solution. Moreover, the rise of pressure produced by increasing the temperature of the sugar solution was the same as what would have been produced by increasing the temperature of the hydrogen gas to an equal amount.

From this it is evident that the molecular weight of a compound may be found, even although it is incapable of existing as gas. It is only necessary to find the quantity of the substance which will, if at the same temperature, and occupying the same volume as 2 parts by weight of hydrogen gas, exert osmotic pressure equal to the ordinary pressure which the hydrogen exerts. There will then be as many molecules of that substance present in solution as of hydrogen in an equal volume ; and the relative weights of the molecules of hydrogen and of the substance will be as 2 to the weight of substance found to exert a pressure equal to that of the hydrogen. To compare with an atom of hydrogen, that weight must be doubled ; for, as before remarked, molecular

weights are compared with the weight of an atom, and not of a molecule, of hydrogen.

The determination of molecular weights by measurements of osmotic pressure, however, is a difficult operation ; and Raoult's discoveries showed how it might be more simply achieved.

It had long been known, that while fresh water freezes at 0°C., salt water can be cooled below that temperature without freezing. Indeed, it has been customary, in order to melt the ice on the streets, to sprinkle them with salt. Raoult made experiments to ascertain the connection between the amount of substance in solution, and the amount of lowering of freezing-point of the solution, and found direct proportionality in many cases. Hence, the lowering of freezing-point of a solution is also proportional to its concentration ; and if we know the number of degrees by which the freezing-point of a substance is lowered by addition of a known weight of a substance of known molecular weight (determined, for example, from its gaseous density), addition of the same number of molecules of some other substance of which the molecular weight is required will produce the same lowering of freezing-point. This can be found by experiment, and the weights of the two substances containing the same number of molecules can then be compared ; and the molecular weights are then proportional to the absolute weights.

Another discovery of Raoult's led to a similar method of comparing quantities containing equal numbers of molecules. The boiling-point of a liquid is raised by the presence of a dissolved substance ; thus, a solution of sugar, syrup, boils at a higher temperature than water. And as before, it was found that equal numbers of molecules in solution brought about an equal rise of boiling-point of the solvent ; and from this observation, a different, though analogous, method for determining atomic weights was deduced.

It soon transpired, however, that these laws hold only for a limited number of substances. Those substances which are known as acids, bases, and salts gave results from which it might have been argued that the molecular weight found in this way was invariably too small. For example, common salt, of which the formula is NaCl (as ascertained by analysis, and by accepting the atomic weights of sodium and chlorine justified by the specific heat argument, and from that founded on gaseous densities), exerted in dilute solution an osmotic pressure twice as great as could have been deduced from its formula. The molecular weight as inferred from the formula is 58·5 ; for Na, 23+Cl, 35·5=NaCl, 58·5. But 58·5 parts of salt in solution were found to exert an osmotic pressure twice as great as the gaseous pressure of two parts of hydrogen, occupying the same volume ; and similarly, that weight of salt was

found to lower the freezing-point, and to raise the boiling-point of its solution double as much as might have been expected.

From what has preceded, it will be seen that the molecular weight of an element or compound can be determined from the vapour-density, or weight in the state of gas ; or from certain other properties which belong to equal numbers of molecules, such as exerting equal osmotic pressure, or equally depressing the freezing-point or raising the boiling-point of a solution. As such properties belong to a " collection " of molecules, they have been termed " colligative."

Let us now consider why an attempt to determine the molecular weight of salt in solution fails. We have seen that substances that dissociate have too low a vapour-density ; and the reason is to be sought in somewhat similar considerations.

It was noticed by Svante Arrhenius, Professor in Stockholm, that solutions of substances which give too low a molecular weight as determined by osmotic pressure, or by rise of boiling-point or depression of freezing-point, are all *electrolytes*, that is, the solutions are conductors of electricity, and are at the same time decomposed. This gave an explanation of the discrepancies observed by Raoult in determining the molecular weights of acids, bases, and salts in aqueous solution, by measuring these constants. For Arrhenius's theory was that in order to conduct electro-

lytically, it was necessary to suppose that such a substance as, say, sodium chloride, of which the formula is NaCl, when dissolved in water, splits up into two portions, each of which acts as a molecule in itself, in its power to exert osmotic pressure, or to produce a rise of boiling-point, or a lowering of freezing-point of the liquid in which it is dissolved. Now, the only possible portions of NaCl are Na (an abbreviation of *natrium*, a word adopted from medieval Latin, to signify the metal in soda or in salt), and Cl, chlorine. But sodium, as we know it, is a soft white metal, which, when placed in water, at once melts, forms itself into a globule, and undergoes the reaction

$$2Na + 2H^2O = 2NaOH + H^2 \; ;$$
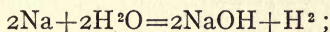
hydrogen is evolved with a hissing sound, and caustic soda, NaOH, remains in solution and gives the water an acrid taste and a soapy feeling. Furthermore, chlorine, as we know it, is a greenish yellow gas, with a strong and easily recognizable smell ; it is soluble in water, to which it communicates its powerful odour. It is clear that a solution of common salt cannot contain either the element sodium or the element chlorine, as we know them. Moreover, if slightly moist chlorine be passed over metallic sodium, great heat is evolved ; the sodium sometimes takes fire and burns in the chlorine, and the product is ordinary white table salt. If sodium and chlorine are

present in a solution of common salt in water, they must be present in some state differing from that of the ordinary elements.

It may be well to pause here for a moment and consider the doubled osmotic pressure exerted by a solution of salt ; twice as much, indeed, as its molecular weight would at first sight render probable ; and also the necessity for believing that it splits into two portions. The case of the density of the vapour of ammonium chloride affords a perfect analogy. It will be remembered that the molecular weight of ammonium chloride is 53·5 ; for $14+4+35·5=53·5=NH_4Cl$; the molecular weight is the sum of the atomic weights. As a molecule of hydrogen consists of two atoms, its molecular weight is taken as 2, the atomic weight of hydrogen being unity. Hence a molecule of ammonium chloride gas, one would expect, should be 53·5/2, or 26·75 times as heavy as a molecule of hydrogen. But as equal numbers of molecules inhabit equal volumes, it follows that the density of ammonium chloride gas should be 26·75 times that of hydrogen. Now, experiment shows that it is only 13·375 times as heavy as hydrogen, if both gases are measured at equal pressure and temperature. But if the density is halved, the volume must be doubled ; for the halving of the density implies that the same weight inhabits double the volume.

Next, reverting to Boyle's Law, which is that if

the volume of a gas be halved the pressure will be doubled, it is clear that if this doubled volume of ammonium chloride gas were made to occupy the theoretical space, the pressure to which it is exposed would need to be doubled. The dissociation of ammonium chloride, then, if it takes place at constant pressure, involves a doubling of the volume ; but if it takes place at constant volume, it involves a doubling of the pressure. The change, $NH_4Cl = NH_3 + HCl$, at constant volume will raise the pressure to twice its original amount. Ammonia, NH_3, and hydrogen chloride, HCl, are, however, well-known gases which exist as such ; and, indeed, they have been recognized in the vapour of ammonium chloride. The case is obviously different with a solution of common salt ; granting that, in order to account for the doubling of the osmotic pressure, it must split into sodium and chlorine, Na and Cl, these substances in salt solution evidently possess properties very different from those which we are in the habit of attributing to them. How can this be accounted for ?

The sodium and the chlorine in a solution of salt in water are not the assemblage of molecules which we call free sodium or free chlorine ; nor are they the atoms Na and Cl. They are *electrically charged atoms* or *ions*, as Faraday termed them. The word " ion " means " wanderer " or " traveller " (literally, " going ") ; this name was given because such atoms charged with positive or negative

electricity move, the positively charged sodium atoms in one direction, the negatively charged chlorine atoms in the opposite direction, when two wires or plates, the one negatively, the other positively electrified, are dipped into the solution. The ions therefore behave like any small charged bodies. If, like the sodium ion, they are positively charged, they are repelled from the positive plate and attracted by the negative plate ; if negatively charged, like the chlorine ion, they are repelled from the negative and attracted to the positive plate. They move or " wander " through the solution in opposite directions ; but all ions do not move at the same speed ; the simple ones, possessing only one or two atoms in the molecule, move relatively faster than the complex ones. In moving, moreover, they are retarded in their speed by friction with the molecules of the solvent ; and as solvents have not all equal viscosity, the rate of travel of the ions varies with the nature of the solvent. These are points, however, which, although in themselves of great interest, do not claim our immediate attention.

It is in virtue of these electric charges that ions of sodium and chlorine possess properties different from those of the free elements. It is in virtue of the charge that it possesses that the sodium ion is not at once attacked by the water. A similar example of protection can be experimentally shown with zinc. A sample of ordinary commercial zinc is at

once attacked by a dilute acid, such as dilute sulphuric acid. But if the piece of zinc is charged with negative electricity, by being made the negative pole of a sufficiently powerful battery, it no longer dissolves ; in fact, if a strong current be passed through a concentrated solution of a salt of zinc, the ions of zinc receive negative charges, and become metal, depositing on the negative plate of the battery.

It may excite astonishment that the electro-positive ions of sodium and the electro-negative ions of chlorine do not, as positively and negatively electrified pith-balls would, approach each other and equalize their charges, and so become electrically neutral. The reason why this does not happen appears to be that the solvent is itself a fairly good non-conductor, and that the ions of sodium and chlorine attract, and are surrounded by water-molecules (if the solvent is water) to such an extent that they cannot touch, so as to equalize their charges. By interposing a non-conducting sheet of glass between a positively and a negatively electrified pith-ball, they do not touch, and do not equalize their charges. However, it must not be supposed that all the molecules of a salt like common salt, $NaCl$, are in the state of ions, $Na+$ and $Cl-$; there is always a certain number in the molecular state, $NaCl$; but this number is diminished, relatively to the number of ions, if the solution be made more dilute ; and conversely, if

the solution be made more concentrated, there is an opportunity for oppositely electrified ions to come into contact, and by neutralizing their charges, to unite into salt-molecules. And if sufficiently concentrated, that is, if there is a sufficient number per unit-volume of solution, molecules of salt separate out in the solid state as crystals. These crystals are practically non-conductors of electricity, and are generally said not to be " ionized." The non-ionized molecules of salt in solution do not carry electricity ; they are not ions ; and as they increase on concentration of the solution, when the protecting water-molecules are removed, the total number of ions of sodium and chlorine is diminished.

The more ions there are in a solution, the better it conducts electricity. It is possible to measure the power which a solution possesses of conducting electricity, or its " conductivity " ; and as conductivity is proportional to the number of ions, the relative number of ions can be measured by measuring the conductivity. The more dilute the solution, the greater the number of ions ; and by measuring the conductivity of a solution of salt, very dilute indeed, it may be assumed that all the molecules are in the state of ions. Or, the conductivity of the salt solution at different concentrations may be measured and plotted on curved paper ; and by prolonging the curve, it may be ascertained what the conductivity would have

been had the solution been infinitely diluted; when all the salt would have been in the ionic state.

As the conductivity is proportional to the number of ions, it is easy to determine the amount of ionization at any particular dilution by measuring the conductivity. For instance, if the conductivity at infinite dilution is 10, and at some particular dilution is 7, it means that of every 10 molecules, 7 are in the state of ions. Now, it must be remembered that these ions behave like molecules in raising osmotic pressure, and in causing depression of freezing-point and rise of boiling-point; hence, if the ionic theory is true, a determination of the relative number of ions can also be made by measurements of these properties. This has been done; with the result that a very satisfactory agreement between all four methods of measuring ionization has been obtained. This concordance affords substantial proof of the correctness of Arrhenius's suggestion that the state of salts, acids, and bases in solution is that of partial or complete ionization, according to the nature of the salt, acid, or base, the nature of the solvent, and the degree of dilution.

We have now to consider the question, what becomes of the ions when the charge is removed; or, in other words, what are the products of electrolysis of acids, bases, and salts. This problem is simplest when the case of fused salts is con-

sidered, for the products are then not liable to be changed in any way by the action of the solvent. It is clear, as already explained, that if the ion of sodium owes its immunity from attack by water to the positive charge which it holds, when the positive charge is removed it will be attacked. Hence, in aqueous solutions, the problem is often obscured by subsidiary changes which take place after the ions are discharged.

When a current of electricity of sufficient strength is passed through molten salt, one of the electrodes, the negative, being a piece of iron wire, and the other, the positive, hard gas-carbon, gas begins to bubble off from the positive electrode. That gas is ordinary chlorine, characterized by its yellow colour and its peculiar odour. At the same time, a film of molten metal adheres to the iron ; when it accumulates it is apt to float up in globules ; each globule takes fire when it reaches the surface of the molten, red-hot salt. To prevent this, it is arranged that the negative iron wire should pass down the centre of a short fire-clay tube, so that the metal, when it floats up, forms a melted layer in the tube, and is exposed to air only at the top ; the oxygen of the air has not then the same chance of coming into contact with the melted sodium, and a little surface oxidation is all that takes place. When a sufficient quantity has accumulated, the current is stopped, and a sort of spoon-shaped iron is placed below the open

lower end of the fire-clay tube; it may then be lifted out of the melted salt, and, after cooling a little, plunged under the surface of paraffin oil, which has no action on metallic sodium. When cold, the sodium may be cut out with a knife.

In this case, as when it was dissolved in water, the salt is partially ionized; the protecting liquid is in all probability the non-ionized, fused salt, which is always present along with the ions of sodium and chlorine, and which does not conduct, but which plays the part of the water in the solution of salt in water, and surrounds the ions, preventing them from discharging into each other. The metal sodium does not alloy with, or attack the iron of the negative electrode; nor does the chlorine act on the carbon of the positive electrode. Sodium may be boiled in an iron vessel; and carbon may be heated white-hot in a current of chlorine, without any action taking place in either case. For this reason, both the ions, when discharged, can be collected in the free state, for they have become ordinary sodium and chlorine.

Why this is not the case when a solution of salt is electrolysed is evident from the following considerations: the element sodium, as already remarked on page 39, attacks water, liberating hydrogen gas, and forming caustic soda, NaOH. As a matter of fact, the caustic soda, or sodium hydroxide, to use the systematic chemical name, is present in solution partly as ions of sodium, $Na+$

and hydroxyl, OH—. Hence what happens when a current is passed through a solution of common salt in water is that no change takes place in the condition of the sodium ions; but the negative charge, which should theoretically convert them into metallic sodium, instead of doing so, is transferred to one of the atoms of hydrogen of the water, and hydrogen is set free, instead of sodium. At the same time, the other group in the water, hydroxyl, OH, acquires a positive charge. Nor does the chlorine come off wholly as gas. A part of it, too, reacts with the caustic soda (unless special precautions are taken to keep them in separate compartments), and yields several products, among which are salts named sodium hypochlorite and chlorate; and at the same time, some common salt is reproduced. So far as the sodium is concerned, the change may be represented by the equation (where Aq stands for Aqua, an indeterminate amount of water) :—

$$Na+.Aq + Cl-.Aq + H+.Aq + OH-.Aq=$$
$$Na+.Aq + OH-.Aq + Cl \quad + \quad H$$
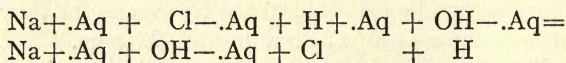
The hydrogen comes off as such; $H+H=H^2$, a molecule of hydrogen as gas. Some of the chlorine also comes off as such; $Cl+Cl=Cl^2$, gaseous chlorine. But some of the chlorine acts on the caustic soda thus :—

$$Cl^2 + 2Na+.Aq + 2OH-.Aq = Na+.Aq$$
$$+ Cl-.Aq + Na+.Aq + OCl-.Aq + H^2O$$
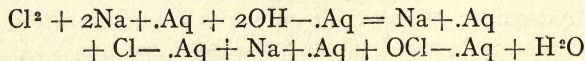
The ions, OCl—, are termed hypochlorite ions ; in combination with Na+, they form the salt NaOCl, which can be crystallized out of the solution by evaporation with special precautions.

This reaction has been considered in some detail, in order to give an idea of the difficulties which beset the study of the electrolysis of solutions of salts.

It has already been remarked that the name " ion " was first used by Faraday, for long Professor in the Royal Institution in London. He also discovered a law of the first importance, dealing with the relative weights of the ions set free by electrolysis ; the law is known by his name. It is : when compounds are decomposed by the same electric current, the relative weights of the ions discharged, and therefore set free, are proportional to the equivalents of these ions. A few instances will render the conception clear.

Common salt, as already remarked, is formed by the action of sodium on chlorine. For every 35·5 parts of chlorine in combination, there are 23 parts by weight of sodium. Now, in hydrogen chloride, 1 part by weight of hydrogen is in combination with 35·5 parts of chlorine ; and for that reason, 35·5 is termed the " equivalent " of chlorine. By passing hydrogen chloride gas over hot sodium, the sodium replaces the hydrogen in the proportion of 23 parts of sodium to 1 of hydrogen. The number 23 is therefore the

equivalent of sodium ; it is the weight of sodium which can replace 1 part by weight of hydrogen. Now, when a current of electricity is passed through melted salt, it is not to be wondered at that they are liberated in these proportions. But if the current, after having passed through the fused salt, is next passed through a solution of iodide of lead, for example, containing ions of lead and of iodine, in the proportion of 103·5 parts of lead to 127 parts by weight of iodine, the weight of lead deposited as metal has the ratio to that of the sodium liberated as metal of 103·5 : 23 ; and of the iodine, 127 parts by weight will be liberated ; this is exactly the amount which will combine with 1 part of hydrogen to form hydrogen iodide, a gas closely resembling hydrogen chloride. In short, all the elements or groups liberated on electrolysis are liberated in quantities proportional to their equivalents.

Turning this statement round, it follows that equivalents of elements or groups of elements convey equal quantities of electricity. Thus, if the quantity of electricity conveyed by 23 parts of sodium is equal to that conveyed by 1 part of hydrogen, by 103·5 of lead, by 35·5 of chlorine, by 127 of iodine, and so on, is equal, it follows that as these numbers are either identical with, or simple fractions of, the atomic weights of these elements, an atom of an element must be able to convey, as an ion, either 1, 2, 3, or 4 unit charges

of electricity. The equivalents of hydrogen, 1 ; sodium, 23 ; chlorine, 35·5 ; and iodine, 127 are identical with the atomic weights of these elements ; that of lead, 103·5, is half its atomic weight, which has been determined by analysis of its oxide ; 103·5 parts by weight of lead combine with 8 of oxygen, that is, replace 1 of hydrogen ; and by its specific heat, which is very nearly 0·03. That agrees with the law of Dulong and Petit, stated on page 26 ; for it is inversely as the atomic weight of lead.

The word " electron " was suggested by Dr. Johnstone Stoney for that quantity of electricity which is conveyed by the equivalent of an element ; it may be termed a unit of electricity. While an atom of hydrogen, or of sodium, is attached to one electron, an atom of lead is attached to two ; and there are instances of elements of which an atom can combine with three and with four electrons. This property is intimately connected with what has been termed the " valency " of the elements.

After Cannizzaro's pamphlet, published in 1858, had convinced chemists of the truth of Avogadro's hypothesis, and true formulæ were made possible, the conception of valency arose. For example, an atom of chlorine or an atom of iodine unites with one atom of hydrogen ; an atom of sodium displaces an atom of hydrogen ; such elements are termed " univalent," or " worth one " atom of

hydrogen. Oxygen and sulphur are examples of elements which combine with two atoms of hydrogen, and are therefore termed " bivalent " ; similarly, copper and lead are bivalent, for one atom of copper or of lead can replace two atoms of hydrogen, as for instance in copper chloride, $CuCl^2$, and lead iodide, PbI^2. Elements may, however, have more than one valency. There is, for example, another chloride of copper, named cuprous chloride, of which the simplest formula is CuCl ; it contains 63·6 parts by weight of copper to 35·5 of chlorine ; 63·6 parts of copper have thus replaced 1 part of hydrogen, and in that compound the equivalent of copper is 63·6. Its valency in that compound is therefore 1. Similarly, we are acquainted with compounds of sulphur, such as SO^2, in which sulphur is quadrivalent, and SO^3, in which it is hexavalent, or capable of replacing six atoms of hydrogen.

CHAPTER IV

THE PERIODIC ARRANGEMENT OF THE ELEMENTS

AFTER the true atomic weights of the elements had been determined, it was for the first time possible to enquire whether there could be found any relation between these numbers ; but it would serve little purpose to describe attempts to reduce them to an orderly scheme before the year 1860, when Cannizzaro showed the scientific world what actual figures should be accepted for these constants. From a much earlier period of the world's history, however, speculations had been common with reference to what was called " the unity of matter " ; Prout, soon after Dalton had propounded his atomic theory, made the suggestion that the atomic weights of the elements were whole multiples of 1, that of hydrogen. This, however, was soon seen to be untenable, although, as we shall see, the central idea that the elements are compound has much to support it.

In 1817, Döbereiner pointed out that the atomic weight of strontium could be approximately calculated by adding together the atomic weights

of calcium, 40, and barium, 137, two allied elements, and dividing by two. The quotient, 88·5, differs from the real atomic weight of strontium, 87·6, by less than a unit. In 1829, he brought forward other instances of the same approximate regularity. Similar attempts were made in 1850 by Pettenkofer ; in 1851 by Dumas ; and in 1857 by Lenssen. Efforts to find other numerical relations between the atomic weights of the elements were made by Kremers, Gladstone, Cooke, Odling, and Strecker, between 1850 and 1860 ; but little light was thrown on the question.

The first hint of a periodic arrangement was given by De Chancourtois in 1862 ; he constructed a cylindrical diagram, in which the atomic weights were taken as ordinates ; the abscissæ were regular numbers so chosen that as the helix made a fresh turn round the cylinder, similar elements appeared on the same ordinates. Thus, lithium and sodium fall on the same vertical ; so do boron and aluminium, nitrogen and phosphorus, and carbon and silicon ; and these pairs of elements exhibit a marked analogy with each other.

In 1863 John Newlands, and in 1864 Lothar Meyer, pointed out that if the atomic weights of the elements be arranged in numerical order, $H=1$, $Li=7$, $Be=9·2$, $B=11$, $C=12$, etc., the eighth element had similar properties to the first, the ninth to the second, the tenth to the third, and so on. This Newlands termed the " Law of

Octaves," from analogy with a musical scale, where the tones are, as it were, repeated on a lower key on descending the scale by eights. Meyer's table represented the same idea more completely ; and in 1869 and 1870 Meyer and Mendeléef independently evolved the scheme which, with more or less modification, is accepted at the present day. We need not enter into a history of these modifications ; it will suffice to give the table in its most modern form, with the most recent determinations of atomic weights.

We are, however, met with a difficulty ; while the elements up to chlorine (35·5) repeat the characteristic properties after an interval of eight elements, the higher members of the series are not so regular in repetition, and the interval is a longer one, 17 elements usually intervening before the element shows analogy with its predecessor. This is perhaps best shown by printing the symbol of such elements to the right of the columns, the two first rows representing what may be termed " elements of short period."

To show fully the reasons why the elements in the various vertical columns are believed to be analogous to each other would involve the writing of a text-book of chemistry. But some peculiarities connected with the table will here be pointed out in their order.

Let us consider, as a first example, the elements on the left side of Column I ; These comprise

I	II	III	IV	V	VI	VII	VIII
H 1·008							He 3·96
Li 6·94	Gl 9·1	B 11·0	C 12·00	N 14·01	O 16·00	F 19·0	Ne 20·2
Na 23·00	Mg 24·32	Al 27·1	Si 28·3	P 31·04	S 32·07	Cl 35·46	A 39·88
K 39·10	Ca 40·07	Sc 44·1	Ti 48·1	V 51·0	Cr 52·0	Mn 54·93	Fe 55·84, Ni 58·68, Co 58·97
Cu 63·57	Zn 65·37	Ga 69·9	Ge 72·5	As 74·96	Se 79·2	Br 79·92	Kr 82·92
Rb 85·45	Sr 87·63	Y 89·0	Zr 90·6	Cb 93·5	Mo 96·0	100 ?	Ru 101·7, Rh 102·9, Pd 106·7
Ag 106·88	Cd 112·40	In 114·8	Sn 119·0	Sb 120·2	Te 127·5	I 126·92	Xe 130·2
Cs 132·81	Ba 137·37	La 139·0, Pr 140·6, Nd 144·3, Sa 150·4, Eu 152·0, Gd 157·3, Tb 159·2, Dy 162·5, Ho 163·5, Er 167·7, Tm 168·5, NY 172·0, Ln 174·0, Ct 176·0	Ce 140·25				
				Ta 181·5	W 184·0	187	Os 190·9, Ir 193·1, Pt 195·2
Au 197·2	Hg 200·6	Tl 204·0	Pb 207·10	Bi 208·0	214 ?	219 ?	Nt 222·4
? 221	Ra 226·4	? 229	Th 232·4	235 ?	U 238·5		

hydrogen, lithium, sodium, potassium, rubidium, cæsium, and an unknown element of atomic weight about 224. Leaving hydrogen for the present, the rest of the elements mentioned are all soft, white metals, very easily inflammable that is, with a great tendency to combine with the oxygen of the air ; they are all violently attacked by water, with evolution of half the hydrogen which they contain and formation of the respective hydroxides, according to the equation :—

$$2M + 2H^2O = 2MOH + H^2.$$
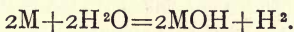
The hydroxides are all white, easily fusible substances, readily soluble in water ; their solutions have a burning " caustic " taste, hence, they are termed " caustic soda," " caustic potash," etc. These hydroxides react at once with acids, forming salts, almost all of which are soluble ; the salts with the same acid have as a rule the same crystalline form. When heated in a flame, the salts impart luminosity to the flame, the flame being turned red by salts of lithium and rubidium, yellow by sodium, violet by potassium, and blue by cæsium. On examining the flames with a spectroscope, so as to analyse the light into its coloured constituents, it is seen in each case to consist of a few brightly coloured lines ; for instance, the spectrum of lithium is characterized by a red line ; that of sodium by two yellow lines very close together, that of potassium by a

red and a violet line, and so on. Indeed, the easiest way of distinguishing between such closely resembling elements is by observing their spectra.

Progressiveness or " periodicity " is also to be noticed in the physical properties of these elements ; lithium has the highest melting-point ; next comes sodium, next potassium ; that of rubidium is still lower, while cæsium melts at a temperature very little higher than that of the atmosphere. The densities of these elements also increases with atomic weight ; lithium is the lightest solid known ; sodium and potassium are lighter than water ; rubidium is heavier, and cæsium is nearly twice as dense as water.

Let us take another instance from another column, that of which the first member is fluorine (VII). The other members are chlorine, like fluorine, a yellow gas, but with a strong admixture of green ; bromine, a red liquid ; iodine, a black solid ; and an unknown element of approximate atomic weight 219. Fluorine, cooled with liquid air, condenses to a yellow liquid ; chlorine liquefies at $-35°$C. ; bromine boils about 60°, changing to a red gas ; and at 184°C. iodine changes to a violet gas. All these elements have analogous odours ; that is, one would refer them to the same class. They are not combustible ; they show no great tendency to combine with oxygen. They all combine with metals ; there are

few metals which resist attack by the " halogens,"
as the members of this group are generically called.
The " halides," the generic name for their salts,
differ according to the nature of the metals which
they contain ; but those of any one class show
close analogies with each other. Thus, with the
metals of the alkalies, lithium, sodium and their
congeners, the fluorides, chlorides, bromides, and
iodides are all white salts, easily soluble in water,
and all crystallize in cubes ; they can all be pre-
pared according to the same scheme, for instance,
by mixing solutions of the hydroxides with
solutions of the compounds of the halogens with
hydrogen, and evaporating to dryness, thus :
$NaOH + HCl = NaCl + HOH$. The compounds of
hydrogen with the halogens are formed directly, by
bringing halogen and hydrogen together ; they are
gases, very easily soluble in water, and the solu-
tions have all a sour taste, a character which has
gained for them the name of " acids."

Similar remarks could be made about the
elements in each of the columns ; it is clear that
by the periodic arrangement elements are brought
together which display marked · analogy with
each other.

It is an open question whether hydrogen should
be placed at the head of the first or the seventh
column ; whether it displays more analogy with
the metals of the alkalies or with the halogens. On
the whole, its analogies with the former are more

marked ; but it appears that there would then be places for six undiscovered elements having atomic weights between those of hydrogen and helium ; and that must be pronounced improbable.

The differences between the atomic weights of the first three elements in each column show some attempt at regularity ; thus, between Li and Na and between Na and K, the difference approaches 16 units ; differences of the same order are found between the atomic weights of glucinum, magnesium, and calcium ; between boron, aluminium, and scandium ; between carbon, silicon, and titanium, and so on. These are elements of short periods. Between potassium, rubidium, and cæsium, the differences are about 46 and 47 units ; between calcium, strontium, barium, and radium, the differences are respectively 46·56, 49·74, and 89·03, or roughly in the proportion of 3, 3, and 6, if the difference between elements of short periods, 16, be taken as unity. Similar considerations would apply to the members of the other columns.

Now, many compounds of carbon and hydrogen are known, termed " hydrocarbons." These are arranged in several series, each series containing compounds similar in physical and chemical properties ; members of such a series are said to be " homologues," and the series is termed a " homologous series." Here is an example :—

HOMOLOGUES OF THE PARAFFINE SERIES

Methane, CH^4	.	16	Hexane, C^6H^{14}	.	86
Ethane, C^2H^6	.	30	Heptane, C^7H^{16}	.	100
Propane, C^3H^8	.	44	Octane, C^8H^{18}	.	114
Butane, C^4H^{10}	.	58	Nonane, C^9H^{20}	.	128
Pentane, C^5H^{12}	.	72			

and so on up to $C^{60}H^{122}$, named di-myricyl. The reason of this regularity is perfectly well known ; it is due to the fact that each atom of carbon, which is a tetrad, is capable of uniting with other atoms of carbon, as well as with hydrogen, so as to form a chain, or it may be branched chains. To illustrate this by a few simple examples, methane is known to consist of an atom of carbon in union with four atoms of hydrogen, and the

$$H-\underset{\displaystyle H}{\overset{\displaystyle H}{C}}-H.$$

structural formula ascribed to it is $H-C-H$. To ethane, the second of the series, the formula as-

$$H-\underset{\displaystyle H}{\overset{\displaystyle H}{C}}-\underset{\displaystyle H}{\overset{\displaystyle H}{C}}-H,$$

cribed is $H-C-C-H$, and to propane, the third,

$$H-\underset{\displaystyle H}{\overset{\displaystyle H}{C}}-\underset{\displaystyle H}{\overset{\displaystyle H}{C}}-\underset{\displaystyle H}{\overset{\displaystyle H}{C}}-H,$$

and so on, each hydrocarbon

differing from its successor by the addition of one carbon and two hydrogen atoms. The atomic weight of carbon is 12, hence this addition involves the increase of the molecular weight by 14, that of the group CH_2; and this is shown in the series of figures which follows the formulæ of the hydrocarbons given above.

The partial analogy of series like this with the columns of elements in the periodic table is striking; they differ, however, inasmuch as the differences in the atomic weights of " homologous " elements is not regular; and also in that the series are not perfect. But the resemblance is sufficient to warrant the guess that the elements may be complex, and built up of simpler substances in some such fashion as the hydrocarbons. We shall see, later on, evidence to justify this guess, although the problem is a complicated one, and the complete solution has not yet been found. The lack of regularity in the differences in the atomic weights of contiguous elements has not yet been elucidated.

In this connection it may be noted that in some cases, in order to place the elements in their appropriate columns, the order of consecutive atomic weights has not been followed; this is the case with argon, 39·88, which precedes potassium, 39·10; and also in the case of tellurium, 127·5, which precedes iodine, 126·92. As yet, no explanation of this necessity is forthcoming.

THE PERIODIC ARRANGEMENT

In the eighth column there are three groups, each consisting of three elements, viz. iron, nickel, and cobalt ; ruthenium, rhodium, and palladium ; and osmium, iridium, and platinum ; this arrangement has been made, because in each of these groups the elements resemble each other strongly, both physically and in the properties and reactions of their compounds. The same is the case with the long group of elements following lanthanum, La, in the table ; these thirteen elements, if distributed along the rows in the order of their atomic weights, would go far to fill the eighteen vacant spaces between cerium, Ce, and tantalum, Ta. It is by no means impossible that there are still five which await discovery ; but they must not be thus distributed ; for if they were, they would in no wise fit in with the properties of the other elements belonging to the columns in which they would fall. Hence they have been placed in a group in the third column, following lanthanum, which they closely resemble, both physically and chemically.

Mendeléef, one of the early authors of the periodic table, found that he could not follow the consecutive order of numbers representing atomic weights, and at the same time place in each column similar elements ; the analogy between silicon, Si, and titanium, Ti, in the fourth column, was too strong to allow of the latter following aluminium in the third column ; and at that time

scandium, Sc, had not been discovered. Nor had gallium, Ga, the fourth member of the third column, nor germanium, the fourth of the fourth column, come to light. He therefore predicted the existence of these then undiscovered elements, foretold their approximate properties, from analogy with their immediate neighbours in the table, and actually gave them provisional names. Thus the element with atomic weight 44 was termed by him " eka-boron " ; that with atomic weight 70, " eka-aluminium " ; and that with atomic weight 72·5, " eka-silicon," from the Sanscrit numeral " eka," one. These elements were subsequently discovered by Cleve, Lecoq de Boisbaudran, and Winckler, who gave them the names by which they are now known.

There are still gaps for new elements of atomic weight 100 and 187 ; one of these is possibly the metal " canadium," of which the discovery has recently been announced. Gaps are more numerous towards the end of the table ; of that, notice will be taken at a later part of this book. Niton, Nt, and radium, Ra, have recently filled two gaps, which were outstanding.

The periodic table serves, in addition to the methods previously mentioned, to give evidence regarding the atomic weights of elements. A case in point is that of beryllium, or glucinum, as it is now called, Gl. Its equivalent is 4·55 ; that is, 4·55 parts by weight of glucinum replace 1 part

of hydrogen, in combining with 35·5 parts of chlorine. Its atomic weight must therefore be that number, multiplied by either 1, 2, 3, or 4, etc. Its similarity with aluminium, both in its physical properties, as well as in the properties of some of its compounds, and a determination of its specific heat (which is abnormal), led to the conclusion that its atomic weight should be $4·52 \times 3 = 13·65$. But an element of that atomic weight cannot find a place in the periodic table ; there is no room for it between carbon (12) and nitrogen (14). Hence the conclusion that its atomic weight is $4·55 \times 2 = 9·1$; a conclusion confirmed by a determination of the vapour-density of its chloride, found to equal 40 ; that value involves the molecular weight 80, and the molecule evidently must consist of an atom of glucinum, $Gl = 9·1$, + 2 atoms of chlorine, $= 2 \times 35·5$, the total adding to 80·1.

The periodic table also suggests the possibility of further discovery. After Rayleigh and Ramsay had isolated argon from air, and Ramsay had found terrestrial helium as a constituent of minerals containing the elements thorium and uranium, the existence of neon, krypton, and xenon as members of the same group was inferred ; and a systematic search by Ramsay and Travers resulted in their separation from atmospheric air, by liquefaction followed by continued fractionation. Rutherford and Soddy, who were the first to draw attention to the escape of an inactive gas

from radium, rightly classed it among the inactive gases; and the investigation of its physical properties by Ramsay and Gray, coupled with the determination of its vapour-density, conclusively proved the justice of its inclusion in the eighth column, and indicated that it forms the last member of the series.

CHAPTER V

ON MAGNITUDES

THE reader has now had presented to him the evidence, in a simple and condensed form, which has led to the inference that matter is discrete, and that it consists of small particles termed molecules ; he has also seen the arguments for the conclusion that molecules sometimes consist of single atoms, but more generally of groups or congeries of atoms, capable of independent existence. The next subject for consideration will be the " Kinetic Theory of Gases," or the theory of gases as revealed by their motion. This theory rests solely on inferences drawn from the behaviour of gases under different conditions of temperature and pressure ; and it enables us to calculate with some degree of probability the size of the molecules, their rates of motion, and other constants of the same nature.

But before entering on these matters, it will be convenient to pass in review the extent of human knowledge regarding magnitudes, or the distances in space accessible to our senses, whether aided by instruments or not. The considerations brought

forward in this chapter are taken chiefly from an essay by the late Dr. Johnstone Stoney, published in 1899.

The unit of measure, now universally adopted among scientific men, is the *metre*. It was originally intended to be one ten-millionth part of the length of the earth's quadrant passing through Paris, that is, the shortest line on the circumference, joining the earth's pole with its equator. But owing to the insufficiency of the measures made by Delambre and Mechain, when it was decided by the French Government that Borda should construct such a standard, it is now known that the bar of platinum, kept at the Bureau des Archives at Sèvres near Paris, differs by a very small fraction from that length. Instead of adopting the results of more recent and more accurate measurements, it has been deemed better to regard the length of that bar as a metre. To convey an idea to those English readers who are not familiar with the metric system, it may be stated that its length is approximately a yard ; more accurately a yard and a twelfth, or 39 inches ; more accurately still, 39·37079 inches. The tenth part of this length, or one decimetre, may be conceived as practically four inches ; the hundredth part, or one centimetre, as $\frac{2}{5}$ of an inch ; and the thousandth part, or one millimetre, as $\frac{1}{25}$ of an inch. The words decametre and hectometre are rarely used ; they express 10 and 100 metres respectively. But

the term kilometre is common ; it is 1000 metres, and is nearly equal to $\frac{5}{8}$ of a mile, or 5 furlongs. And 1600 metres differ from a mile by only one two-hundredth part.

Measures of surface, with which we shall have less to do, are derived by taking as units the squares of the measures of length. Thus, a square metre contains 100 square decimetres, and as each square decimetre contains 100 square centimetres, $100 \times 100 = 10,000$ square centimetres. Similarly, as there are 100 square millimetres in a square centimetre, there are 10,000 in a square decimetre, and a million ($=100 \times 10,000$) in a square metre.

The units of volume are constructed of cubes of which an edge is a unit of length, and a surface a unit of area. Thus, a cubic metre contains 1000 cubic decimetres ; 1000×1000, or a million cubic centimetres ; and $1000 \times 1000 \times 1000$ or a thousand million cubic millimetres. One cubic decimetre is termed a litre.

For units of weight, the weight of water, capable of filling a cubic centimetre exactly at 4°C., has been chosen. The temperature 4° has been fixed on, because at that temperature water possesses its greatest density, or occupies its smallest volume. The behaviour of water as regards temperature is anomalous. When water at 0°, obtained by melting ice, is warmed, it does not expand, as nearly all other liquids do ; but it contracts steadily until the temperature 4° is

reached ; it then begins to expand, and continues to expand with rise of temperature. The weight of one cubic centimetre or " 1 cc." of water at 4°C. is termed a gram ; 1000 grams, the weight of a cubic decimetre of water at 4°, is named a kilogram. Its weight is nearly $2\frac{2}{5}$ lbs. avoirdupois. Now, as 10 lbs. of water exactly fill a gallon measure, there are in a gallon $\dfrac{10}{2\frac{1}{5}}=4\cdot54$ litres, or in round numbers, $4\frac{1}{2}$ litres. As a gallon contains 4 quarts, a quart $=\dfrac{4\frac{1}{2}}{4}=1\frac{1}{8}$ litre, or a quart is an eighth more than a litre. A pint is therefore an eighth more than half a litre, or 562 cubic centimetres.

To return to weights : as there are 16 ounces in one pound, and $2\frac{1}{5}$ lbs. in one kilogram, there are $(16\times2\frac{1}{5})$ oz. in a kilogram, or nearly 35 ounces ; and there are nearly 28 grams in an ounce ; and 1 gram $=15\cdot432$ grains, a number easily remembered, because of the sequence 5432. The thousandth part of a gram, or 1 milligram, is the thousandth part of $15\cdot432$ grains, or $0\cdot0154$ grain, or about $\frac{1}{65}$ of a grain.

So much for the units of measure. As we shall have to deal, however, with very large numbers as well as with very small fractions, attention must be directed to a device which has come into use largely within the last few years, owing to the necessity of such widely divergent magnitudes as

have been introduced recently into science, and which renders arithmetical conceptions and operations much more simple.

The principle of the notation is based on powers of 10. These may be either positive $(+)$ or negative $(-)$. The positive powers represent numbers greater than 1; the negative ones, smaller numbers. Ten squared, or 10^2 is 100; 10^3 is 1000, and so on. By convention, 10^1 or " ten to the first power " stands for 10, and 10^0 for 1, unity; 10^{-1}, or " ten to the power minus one," for one tenth $\frac{1}{10}$; 10^{-2} or " ten to the power minus two," is $\frac{1}{100}$th (one-hundredth), and so on. The values of this method of representation will be seen in the table which follows :—

$$10^0 = 1 \qquad\qquad 10^1 = 10$$
$$10^{-1} = 0 \cdot 1 = \tfrac{1}{10} \qquad 10^2 = 100$$
$$10^{-2} = 0 \cdot 01 = \tfrac{1}{100} \qquad 10^3 = 1000$$
$$10^{-3} = 0 \cdot 001 = \tfrac{1}{1000} \qquad 10^4 = 10{,}000$$
$$10^{-4} = 0 \cdot 0001 = \tfrac{1}{10000} \qquad 10^5 = 100{,}000$$
$$10^{-5} = 0 \cdot 00001 = \tfrac{1}{100000} \qquad 10^6 = 1{,}000{,}000$$
$$10^{-6} = 0 \cdot 000001 = \tfrac{1}{1000000} \qquad 10^7 = 10{,}000{,}000$$

$$10^8 = 100{,}000{,}000, \text{ a hundred million}$$
$$10^9 = 1{,}000{,}000{,}000, \text{ a billion}$$
$$10^{10} = 10{,}000{,}000{,}000, \text{ ten billions}$$
$$10^{11} = 100{,}000{,}000{,}000, \text{ a hundred billion}$$
$$10^{12} = 1{,}000{,}000{,}000{,}000, \text{ a trillion}$$
$$\text{etc.} \qquad\qquad \text{etc.}$$

If the number required does not coincide with any

of these, it is represented by a factor; thus, $2 \cdot 8 \times 10^{-8}$ is a two-point-eight hundred millionth or a 28 billionth; $3 \cdot 7 \times 10^9$ is $3 \cdot 7$ billion, or 3 billion, 700 million, and so on.

If we wish to divide one of these numbers by another, we subtract the index, as the power of ten is called, of the divisor from the numerator, to obtain the quotient. Thus, for example, to divide ten billion, or 10^{10} by one-hundred-thousand, or 10^5, we subtract 5 from 10; the remainder 5 is the index of 10^5, or 100,000. Suppose we wish to divide 10^8, or one-hundred-million, by one-thousandth, or 10^{-3}, we subtract -3 from $+9$; the remainder is $+12$, and 10^{12} is one trillion.

Should there be other factors, for example if we have to divide $2 \cdot 5 \times 10^{10}$ by 5×10^{15}, we proceed as follows: subtract 15 from 10; the remainder is -5; next, divide 2, 5 by 5; the quotient is $0 \cdot 5$; hence the answer is $0 \cdot 5 \times 10^{-5}$ or 5×10^{-4}, or in words, five ten-thousandths, or $\frac{1}{2000}$.

It may be of assistance, in realizing this method of numeration, to notice that the index for multiples of ten is always identical with the number of o's which follow the 1; thus, 10^{10} is 1 followed by ten o's; and for fractional numbers the number of o's is always one fewer than the number of o's which precede the 1; thus, 10^{-4} has three significant o's before the 1, besides the o preceding the decimal point, and represents in all four o's, $0 \cdot 0001$, or $\frac{1}{10000}$. The number of o's, in-

deed, is the same as that in the denominator of the vulgar fraction. It is usual to name these magnitudes in a rather cumbrous fashion ; thus, 10^5, or 100,000 metres, is generally named " ten to the fifth power, in metres " ; 10^{-5}, or $\frac{1}{100000}$ of a metre, " ten to the minus fifth of a metre." Dr. Stoney has proposed a much less cumbrous nomenclature. All decimal multiples are expressed in words terminating in " o." For example, a " uno-eight " means the eighth member of the series ; it is 10^8 or 100,000,000. Similarly, that number of metres is termed a " metro-eight." For fractions, it is recommended that the syllable " et " shall be affixed to the number ; thus, a " tenthet-metre " is 1^{-10} metres, or 0,000,000,000,1 metre. This is analogous to such expressions as a " half-pound," a " quarter-inch."

When we survey the various magnitudes with which we are acquainted in Nature, whether by the aid of our eyes alone or by eyes aided by instruments, we find that in both directions there is a limit ; not, indeed, to our powers of thought, for in a numerical respect our powers are infinite ; but in actual fact we are limited, on the one hand, by the distance of the farthest fixed star ; on the other, by the diameter of an electron. Now, Dr. Stoney has introduced a convenient classification of these magnitudes, which is here reproduced with some alterations and additions on the next page. The base or starting-point in this scheme

Total range of vision, aided by the telescope and the microscope

Unknown.

Distances of Nebulæ and Stars.
- Surmised distance of some nebulæ = 10^{19} kilometres.
- Surmised distance of some Stars = 10^{16} kilometres.
- Distance of 61 Cygni 6.4×10^{14}
- Distance of Nova Cygni 3.2×10^{14} kilometres.

Distances of Planets from the Sun.

Neptune	4.5×10^9 kilometres.	
Uranus	$2.8 \times$,,	,,
Saturn	$1.4 \times$,,	,,
Jupiter	7.8×10^8	,,
Mars	$2.3 \times$,,	,,
Earth	$1.5 \times$,,	,,
Venus	$1.1 \times$,,	,,
Mercury	5.8×10^7	,,

Distances of Satellites from their Planets.
- Japetus from Saturn 3.67×10^6 kms.
- Moon from Earth 3.85×10^5 kms.

Geographical Distances.
- Circumference of Earth = 4×10^7 metres
- Diameter of Earth = 12.73×10^6 ,,
- Degree of Latitude at 45° = 1.11×10^5 ,,

Height of Mountains, Houses, Trees, Man, and Animals.
- Height of Ben Nevis = 1.43×10^3 ,,
- Height of St. Paul's = 1.31×10^2 ,,
- Height of a man = 1.8×10^0 ,,

Total range of microscope.
- About smallest distance visible with unaided eye.

1. Wave-lengths of Light.
2. Mean free paths of Molecules at Atmospheric pressure.
3. Average spacing of Molecules in air.
4. Average spacing in solids and liquids.
5. Vibrations of Atoms.

7. Dimensions of Electrons.

8. Unknown.

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	10^{23} Metre	Uno-twenty Kilometre $= 10^{20}$ Kilometre
	10^{22} Metre	10^{19} Kilometre
	10^{21} Metre	10^{18} Kilometre
	10^{20} Metre	10^{17} Kilometre
	10^{19} Metre	10^{16} Kilometre
	10^{18} Metre	10^{15} Kilometre
	10^{17} Metre	10^{14} Kilometre
	10^{16} Metre	10^{13} Kilometre
	10^{15} Metre	10^{12} Kilometre
	10^{14} Metre	10^{11} Kilometre

Stellar Distances,

$10,000,000,000,000 = 10^{13}$	Uno-ten Kilometre $= 10^{10}$ Kilometres.
$1,000,000,000,000 = 10^{12}$	Decamyriaquadrant $= 100,000$ quadrants.
$100,000,000,000 = 10^{11}$	Myriaquadrant $= 10,000$ quadrants.
$10,000,000,000 = 10^{10}$	Kiloquadrant $= 1000$ quadrants.
$1,000,000,000 = 10^9$	Hectoquadrant $= 1,000,000$ Kilometres.
$100,000,000 = 10^8$	Decaquadrant $= 100,000$ Kilometers.
$10,000,000 = 10^7$	Quadrant of Earth's Circumference.
$1,000,000 = 10^6$	Kilokilometre $= 1000$ Kilometres.
$100,000 = 10^5$	Hectokilometre $= 100$ Kilometres.
$10,000 = 10^4$	Decakilometre $= 10$ Kilometres.
$1000 = 10^3$	**Kilometre $= 1000$ Metres.**
$100 = 10^2$	Hectometre $= 100$ Metres.
$10 = 10^1$	Decametre $= 10$ Metres.
$1 = 10^0$	**Metre.**

Distances of Planets and Satellites; geographical distances.

$0 \cdot 1 = 10^{-1}$	Decimetre $=$ First Metret
$0 \cdot 01 = 10^{-2}$	Centimetre $=$ Second ,,
$0 \cdot 001 = 10^{-3}$	Millimetre $=$ Third ,,
$0 \cdot 0001 = 10^{-4}$	Millidecimetre $=$ Fourth Metret.
$0 \cdot 00001 = 10^{-5}$	Millicentimetre $=$ Fifth ,,
$0 \cdot 000001 = 10^{-6}$	Micron $=$ Sixth ,, " μ "
$0 \cdot 0000001 = 10^{-7}$	Decimicron $= 1$ Tenthet Kilometre.
$0 \cdot 00000001 = 10^{-8}$	Centimicron $=$ Eighth Metret.
$0 \cdot 000000001 = 10^{-9}$	Millimicron $=$ Ninth ,, " $\mu\mu$ "
$0 \cdot 0000000001 = 10^{-10}$	Decimillimicron $=$ Tenth ,, Ångström Unit.
$0 \cdot 00000000001 = 10^{-11}$	Centimillimicron $=$ Eleventh Metret.
$0 \cdot 000000000001 = 10^{-12}$	Millimillimicron $=$ Twelfth ,,

Lengths used in Commerce and Laboratory; microscopic distances.

for the numeration of high quantities is the kilometre. Proceeding upwards, we have first such distances as we measure on this earth, as a rule, in Great Britain and America, in English miles. Thus, a degree of latitude, at latitude 45°, is 69 miles $= 1 \cdot 11 \times 10^2$, or 111 kilometres. The distance from Liverpool to New York, roughly 2000 miles, is approximately $3 \cdot 2 \times 10^3$ kilometres. The diameter of the earth is $12 \cdot 73 \times 10^3$ kilometres, or 7918 miles. The circumference of the earth is this number multiplied by π, the Greek letter adopted to denote the ratio of the circumference to the diameter of a circle; its value is $3 \cdot 14159 \ldots$ If we perform this multiplication, we obtain the figure 4×10^4 kilometres, or 4×10^7 metres; that is, 40,000,000 metres, and it will be remarked that the metre is based on the length of the earth's quadrant, being 1 ten-millionth part thereof.

Still proceeding upwards on the scale of measurements, we should have to direct our vision beyond the earth. The nearest object is the moon, at a distance of 239,000 miles, or $3 \cdot 85 \times 10^5$ kilometres. Other satellites are in some cases nearer their planets; Phobos, one of the satellites of Mars, is only 5800 miles, or $9 \cdot 3 \times 10^4$ kilometres, from Mars; the distance of Japetus from Saturn is the greatest distance of a satellite from its planet; it is 2,280,000 miles, or $3 \cdot 67 \times 10^6$ kilometres.

The distances of the planets from the sun all range between that of Mercury and that of Nep-

tune. The figures given in the table refer to the mean distances; for all the planets travel in elipses round the sun. Mercury is a comparatively long elipse, and Neptune an elipse almost approximating to a circle. Those mean distances range from $5 \cdot 8 \times 10^7$ to $4 \cdot 5 \times 10^9$ kilometres.

If we follow the scale of measurements downwards, the decimetre and centimetre call for no special remark. But the millimetre, the 25th of an inch, may be taken as the maximum distance for which a microscope is convenient. The tenth, or even the twentieth part of a millimetre is easily distinguished by the naked eye; the latter is equal to the 500th part of an inch. The thousandth part of a millimetre, designated by the Greek letter μ (mu), is easily seen by aid of a good microscope; the wave-length of light varies from about half this magnitude to about one-twentieth. By help of the " ultra-microscope," in which the objects to be seen are very powerfully illuminated from the side, the fact of their existence can be observed, but owing to the nearness of their magnitude to that of the wave-length of light which illuminates them, it is not possible to determine their form. For instance, the colour of ruby glass is due to the presence of very minute particles of metallic gold; it is possible, by means of an ultra-microscope, to detect the presence of such particles and even to count their number, but not to determine their form; they actually appear to be spherical, but

it must be noted that this may be due to the inter-ference which they exert on the light-waves with which they are illuminated. The shorter the wave-length of the light by which they are viewed, the more distinct they appear, provided luminosity be sufficient.

Such are the ranges of distance accessible to the unaided or aided sight ; smaller magnitudes are the result of *deductions* from measurements.

CHAPTER VI

MOLECULES AND THEIR PROPERTIES

AS remarked in Chapter I, we have agreed to
assume provisionally that matter exists ;
that is, that there is a substratum of " stuff "
underlying the properties which affect our senses.
This matter possesses *inertia ;* if in motion, it re-
sists attempts to alter its velocity ; if at rest, it is
necessary to apply *force* to set it in motion. This
property, which is used theoretically to measure
its quantity, is termed *mass*. Every portion of
matter in the universe attracts (for some unknown
reason) every other portion of matter ; the attrac-
tion varies inversely as the square of the distance
between any two pieces of matter under considera-
tion ; and it is directly proportional to their
masses, or proportional to the product of the
numerical values of their masses. It is reasonable
to suppose that at a given distance a piece of
matter of twice the mass of another will exert
twice the attractive power ; and it is not difficult
to show that if the attraction at distance 1 be taken
as 1, the attraction at distance 2 is $\frac{1}{4}$. In symbols,

$$A = \frac{M_1 \times M_2}{D^2} \times F.$$

(A is attraction, M_1 and M_2 the two masses, D^2 the square of the distance between them, and F a factor, so as to make the right-hand expression numerically equal to A.) It may be remarked in passing that when the earth is one of the attracting bodies we term the attraction *gravity;* and we can compare the masses of any two bodies by weighing them, although no one knows why this attraction should be proportional to the masses.

It has also, as we have seen, been agreed that matter is not continuous, but discrete ; that is, it consists of small particles to which the name "molecules" has been applied. Sometimes a molecule is difficult to subdivide ; in that case it is termed an atom. Sometimes, and this is more generally the case, a molecule consists of several atoms, forming a relatively stable grouping.

It is also believed that molecules, when grouped together regularly in large numbers, with little power of individual motion, build up crystalline solids. The form of the crystals is due to the particular manner in which the molecules are arranged. A crystalline solid may be likened to a regiment of soldiers in, say, a square ; the men keep their relative positions, and, although they retain their power of individual motion to some extent, yet they cannot move relatively to their neighbours. In a solid, every molecule attracts every other ; this form of attraction is known as cohesion, but its precise nature has not yet been discovered.

The solid condition is known as "a state of matter."

Another state of matter is the condition of liquids. Here the molecules have the power of changing their places relatively to each other; but in doing so, as they are closely packed, there is much friction; hence the path of any individual molecule is a slow one. If, in comparing liquids with each other, one is found to flow more easily than another, it is said to possess greater "fluidity"; slowness in flowing is termed "viscosity," and liquids like honey or glycerine are said to be viscous. The passage of one molecule among its neighbours is attended with much friction; this is probably the remains of the directive attraction which causes solids to cohere. The best analogy to a liquid is a crowd of men, all striving to change their places, but hindered from doing so by the fact that each man has to jostle his neighbours before he can make way through the crowd. There is no regular arrangement of molecules in a liquid, as a rule, though some rare liquids are known in which some structure can be detected.

When a liquid is cooled its viscosity increases; not merely is the rate of motion of its molecules decreased, but their frictional retardation increases too. Some liquids—in fact, practically all pure liquids—when cooled to a sufficiently low temperature, change into crystalline solids; their molecules arrange themselves in symmetrical order. If

a liquid is a mixture, however, of two or more liquids, crystallization on cooling may not take place ; the presence of the one kind of molecules prevents the other kind of molecules from finding each other and building up crystals. The viscosity then increases as the temperature is lowered ; and it may become so great that many months or years, or even centuries, may be required before any sign of flowing is detectable. For instance, sealing-wax is generally regarded as a solid. When struck, it breaks with a shell-like or conchoidal fracture ; but if left alone for years a stick of sealing-wax will settle down and form a pool, losing its shape, just as a liquid does. An easy way of showing this quickly is by placing a stick of sealing-wax between two supports, so that it lies horizontally, resting merely on its ends ; in four or five hours it will have sagged and taken the shape of a bent bow.

The third state of matter is termed the gaseous one. In gases, molecules have a rapid rate of motion ; the higher the temperature, and the lighter the gas, the more rapid. The distance between the molecules in a gas is, on the average, considerable ; much greater than in the case of liquids or solids. One cubic inch of water, for example, at its boiling-point, expands into about 1700 cubic inches of steam at the same temperature ; now, if we compare the relative volumes of the two cubes, we shall see that if the edge of one

is 1 inch, the edge of the other is the cube-root of 1700, or about 12 inches. In steam, therefore, the molecules are about twelve times as far apart as they are in water. The condition of affairs, if we apply our analogy, is somewhat ludicrous ; we are to suppose a crowd of men in the corner of a field. For some reason, possibly connected with a " hot " dispute, they separate, and each runs at a great speed in a straight line, regardless of his direction. He pursues his course until he collides against an obstacle—it may be one of his fellows ; if so, he knocks against him and rebounds, pursuing his path with freshly acquired ardour in a new direction ; it may be against the paling which bounds the fields ; when he hits it he again rebounds, the angle of reflection being equal to the angle of incidence ; and so he pursues his path for ever, unless he " cools," and resumes the liquid state.

Very remarkable results have been attained by considering the molecules of a gas as if they were hard elastic spheres, like minute billiard balls. Such considerations are involved in the kinetic theory of gases, or the theory of gases in motion, not as a whole, but as to their molecules. It is not advisable, however, in a book of this kind to give more than a general statement, which will enable the reader to gain an idea of *how* gaseous matter is conceived.

The first consideration is evidently that, considering the erratic paths of each molecule and

their immense number, the task of tracing their behaviour would appear to be hopeless. Astronomers can work out the course of the moon as affected by the earth ; but the problem of " three bodies " is regarded as almost insoluble. How about the problem of myriads of molecules pursuing erratic paths ?

Clerk Maxwell solved this difficult problem. To do so he had to make certain assumptions : first, that the molecules are spherical ; two spheres can collide in only one way, whereas bodies of other shapes can touch in an infinite number of ways. Second, the spheres were supposed to be hard and elastic ; the collisions last only an infinitesimal time, and the sphere was supposed to be incapable of deformation, else vibratory motion in each individual sphere would be set up. Third, they were assumed to inhabit the space in which they moved sparsely, so that collisions between more than two molecules at a time became very improbable. Fourth, they were supposed to be almost infinite in number, because a statistical method was employed, and statistics are true only when very large numbers are considered. Fifth, they were supposed not to be influenced by attraction or repulsion ; no doubt they are, like all other matter, subject to gravitational attraction, but that force was regarded as so feeble as to be negligible. Lastly, they were assumed to be perfectly smooth, so that if a grazing collision were to occur,

they would not rotate; in the language of billiards, they were supposed to be incapable of taking on "side." Having made these assumptions, Clerk Maxwell developed a mathematical expression, enabling him to calculate the average velocity of the molecules. From this, a curve can be constructed, showing that of 10,000 spheres 161 will have a velocity equal to one quarter of the mean velocity; 1120 will have velocities less than half the mean velocity; 5330 will be moving with the average, and with lower, velocities; while 9829 will be moving with velocities less than twice the average. Only about 1 sphere in 20,000 will move with three times the average velocity; the chance of a sphere moving with ten times the average velocity is the incredibly small number 10^{-53}, i.e. 1 followed by 53 noughts.

The two fundamental conceptions of the kinetic theory of gases are, first, that its pressure is caused by the impacts of molecules on the walls of the vessel containing the gas; and second, that temperature is closely related to the rate of motion of the molecules; a higher temperature implying increased, a lower, diminished velocity.

If a mass M is moving with velocity C, the product of the two numbers representing quantity of mass and intensity of velocity, MC, is termed "momentum." If the mass impinges on an elastic surface, each impact will impart momentum equal to 2MC, for the mass parts with velocity C

at the moment of impact, and yet receives equal velocity on leaving the struck surface.

Suppose the mass to be a molecule ; and that a cubical vessel is filled with such molecular masses, whose number is n. To find the pressure on the walls of the cubical vessel, due to the impact of all the molecules, the momentum of each impact must
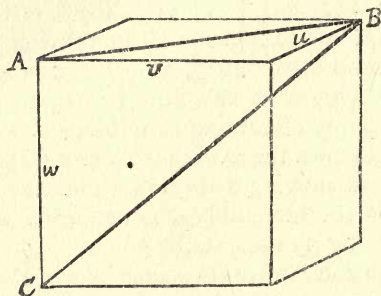
Fig. 1.

be multiplied by the number of impacts in unit time, and by the number of the molecules. But motion takes place in all possible directions, and very few impacts fall normally on the walls. It is possible by the parallelogram of motion, however, to resolve these motions into three directions at right angles to each other, and to deduce from them an average velocity. Let u, v, and w be the com-

ponent velocities at right angles to the plane of the paper, and in the two directions parallel to it. Then $u^2+v^2=(AB)^2$, and $(AB)^2+w^2=(CB)^2$; hence $u^2+v^2+w^2=(CB)^2=C^2$, where C^2 is the resultant velocity. (C may be taken to stand for " celerity.")

Let us consider a single molecule. Its component of velocity, u, leads to the pressure $2mu\dfrac{u}{l}$ $2mu$ being its momentum, and u/l being the number of impacts in unit time, where l is the length of one side of the cube ; for the number of impacts is proportional to the velocity, and inversely proportional to l, the distance which has to be covered between two blows. Hence on two opposite faces the pressure is represented by the sum of $2mu^2/l$, and on the other two pairs of opposite faces, the sum of $2mv^2/l$ and $2mw^2/l$; and the total action is the sum of $2m(u^2+v^2+w^2)l$ =the sum of $2mC^2/l$. The whole surface of the cube is exposed to a pressure of $2mnC^2/l$, for multiplication by n gives the pressure due to all the molecules. To find the pressure on unit area, conceived to be one face of the cube, it is necessary to divide by $6l^2$, for a cube has six faces, and the area of each face is l^2. Hence,

$$p=mnC^2/3l^3,$$

and as l^3 is the volume of the cube, v,

$$p=mnC^2/3v ; \text{ or } pv=\tfrac{1}{3}mnC^2.$$

Now, all the values on the right-hand side of the equation are constant, for the mass of the molecules does not vary, nor does their number, seeing that they are supposed to be contained in a closed vessel ; nor does their velocity vary, for their temperature is supposed to remain constant, and the theory implies that alteration of velocity is caused by alteration of temperature. Thus we arrive at Boyle's Law, which is $pv = $ constant, or, the volume is inversely as the pressure, or $pv = $ constant$/v$.

Temperature, according to this theory, is regarded as the result of the kinetic energy of the molecules, depending on their mass, and on the square of their velocity ; for if the volume is kept constant, and the temperature is increased, the pressure is proportionately increased. Equal rise of temperature produces equal increase of kinetic energy ; and this is approximately true of all gases.

Let C_1 and C_2 be the velocities of the molecules of one gas at temperatures t_1 and t_2, and C'_1 and C'_2, those of another gas ; then,

$$mC_1{}^2/2 = m'C'_1{}^2/2 \ ; \ \text{and} \ mC_2{}^2/2 = m'C'_2{}^2/2 \ ; \ \text{hence,}$$
$$mC_1{}^2/2 : mC_2{}^2/2 :: m'C'_1{}^2/2 : m'C'_2{}^2/2 \ ;$$

that is, the ratio between the kinetic energies of two different gases is the same at corresponding temperatures.

In the equation, $pv = \frac{1}{3}mnC^2$, p, v, and C depend

on temperature, and p, v, m, n, and C on the nature of the gas. And as $pv = \frac{1}{3}mnC^2$, $3pv/2n = mC^2/2$; and substituting,

$$3p_1v_1/2n : 3p_2v_2/2n :: 3p'_1v'_1/2n : 3p'_2v'_2/2n;$$

or more simply,

$$p_1v_1/p_2v_2 = p'_1v'_1/p'_2v'_2;$$

that is, for equal changes of temperature, the change of the numerical value of the product pv alters for all gases in the same ratio. This is Gay-Lussac's Law in its most general form. If we keep p constant, we get the usual statement, that all gases undergo equal change of volume on equal change of temperature.

If two gases are at the same temperature and under the same pressure, the average momentum of the molecules of each must be equal; or,

$$mC^2/2 = m'C'^2/2.$$

If the volumes of the gases are also equal,

$$^2/_3nm/2C^2 = {}^2/_3n'm'/2C^2;$$

hence $n = n'$; that is, under equal conditions of temperature and pressure, equal volumes of gases contain equal numbers of molecules. Now, the molecules consist of small whole numbers of atoms; and as the above law holds for new gaseous molecules formed during any chemical reaction, the proportions in which any two gases

act on each other must be simple. This was proved by Gay-Lussac, long before the kinetic theory was imagined; and the theory, embracing all the facts, lends additional probability to the view.

But the kinetic theory leads us farther. It is possible by its help to calculate the average velocity of molecules of all gases at definite temperatures; and, furthermore, the prediction can be controlled by experiment.

The mass of any gas can be measured by weighing it, and the pressure which it exerts can be ascertained by a pressure-gauge, or manometer; hence from the equation, $pv = \frac{1}{3}mnC^2$, by substituting figures for symbols, the average velocity of a molecule can be calculated.

For helium, for example, the calculation can be made thus: Experiment shows the density of helium, compared with that of oxygen at the same pressure and temperature, to be in the ratio of 2 to 16; it will be remembered that the density of oxygen is expressed by the same number as its atomic weight, and that the latter is the standard, and is taken as 16; and 16 grams of oxygen occupy 11,200 cubic centimetres at 0° and 760, which are agreed on as normal temperature and pressure. One gram of helium, therefore, occupies 11,200/2, or 5,600 cubic centimetres. The pressure corresponding to 760 millimetres, or 76 centimetres, of mercury is in grams $76 \times 13 \cdot 596$, the last number being the density of mercury; the product is

1033·2 grams. But it is necessary to convert grams into dynes; that is done by multiplying by the gravitation constant, expressing the distance which a falling body would traverse per second, were it to continue the rate which it possesses at the end of the first second of fall; in this latitude, it is about 981 centimetres. The product, $1033·2 \times 981 = 1,013,600$ dynes, or units of force. The mass of the gas is the mass of one molecule, m, multiplied by the number of molecules n, i.e. mn.

Transposing the equation $pv = \frac{1}{3}mnC^2$, to $3\frac{pv}{mn} = C^2, C = \sqrt{3\frac{pv}{mn}}$; and substituting figures for symbols, we have $C = \sqrt{\frac{3 \times 1,013,600 \times 5,600}{1}}$; hence C, the average velocity of a molecule of helium at 0° and 760 millimetres pressure is equal to 130,660 centimetres, or 1·3066 kilometre per second. This is somewhat less than half a mile a second. But it must be remembered that no molecule of helium ever traverses half a mile in one direction; it is continually colliding with other molecules, and having its motion interrupted. Supposing, however, that the motion of the molecules were unimpeded, their average distance travelled in one second would be approximately half a mile.

In general terms, as $\frac{mn}{v}$ represents density

compared with water at 4°C., or d ; and as velocity.

$$C = \sqrt{3\frac{pv}{mn}}, \text{ or } \sqrt{3\frac{p}{d}},$$ the average velocity of a

molecule of any gas is inversely proportional to the square root of the density of the gas. This is a law known by the name of Thomas Graham, its discoverer; and his measurements corroborate the kinetic theory, as may be seen by reference to the accompanying table.

Gas.	$\sqrt{d}$.	Reciprocal of the velocity found.
Air	1·000 . . .	1·000
Hydrogen . .	0·263 . . .	0·277
Oxygen . . .	1·051 . . .	1·053
Nitrogen . . .	0·986 . . .	0·984
Carbon dioxide .	1·237 . . .	1·218
Carbon monoxide	0·984 . . .	0·987
Nitrous oxide .	1·237 . . .	1·199

The agreement is good; and it must therefore be concluded that when a gas moves about in a vessel closed with a stopper perforated with innumerable minute orifices, the chance of escaping through these orifices depends on the velocity of the molecules, the more rapidly moving molecules of a gas of low density making a greater number of impacts on the porous stopper, and consequently running a proportionately greater chance of escaping through the pores out of the vessel.

Enough has been said to show that by treating

molecules in the gaseous state as if they were small hard spheres like minute billiard balls, moving through space, and applying to them the ordinary laws of motion, deductions can be drawn which are in complete harmony with what is known of the behaviour of gases as regards temperature, pressure, and volume ; and that the rate of motion of the molecules, calculated from the kinetic theory of gases, gives results capable of confirmation by experimental means. But we have omitted to mention many other properties of gases which can equally well be explained and confirmed numerically by similar processes of reasoning on the same assumptions ; it is possible to calculate the average free path of a molecule, that is, the average distance which a molecule of any particular gas at a known temperature and pressure must traverse before colliding with another molecule. For instance, for oxygen that distance is 94.6×10^{-6} centimetre, or approximately the ten-thousandth of a centimetre. Knowing the average free path, and also the average velocity per second of a molecule, the average number of collisions which a molecule makes in a second can also be calculated ; for oxygen it is 4.4×10^{9}, or nearly $4\frac{1}{2}$ trillion per second.

Such a calculation assumes that collisions take place at the centres of the molecules, which is an absurd supposition, for they must evidently touch at their surfaces, not their centres. The number

of collisions will actually be greater than that given ; because the distance traversed between two collisions will be shorter by the diameter of a molecule (or two half diameters, thus : ○——○ instead of ⊝——⊝) than that calculated. This makes it possible to estimate the diameter of a molecule, and from that figure its mass. But of this more hereafter.

We have learned, then, that not merely is the existence of molecules and atoms to be inferred on chemical grounds, but also that the physical behaviour of gases lends the hypothesis great support.

In the next chapter an account of recent researches will be given which may be said to demonstrate the existence of molecules, inasmuch as visible masses can be observed to comport themselves in a manner identical with what has been postulated regarding invisible molecules.

CHAPTER VII

VISIBLE "MOLECULES"

SO far as we have gone, the existence of atoms and molecules has been deduced from reasoning based on the physical and chemical behaviour of elements and compounds; and it has been shown that on the supposition that gaseous matter is composed of small discrete particles, in other words of molecules, the behaviour of the gas as a whole as regards pressure, temperature, and volume is in accordance with that supposition. But of recent years it has been found by various observers that particles of matter, visible under high microscopic powers, display properties which resemble in most respects those of actual molecules; although the visible particles must consist of groups of molecules, and are enormously greater in size than any molecule, even the largest known.

The development of the microscope made great strides about the beginning of last century; and the botanist Robert Brown, immediately after the use of achromatic objectives had been introduced, noticed that small particles of dust, or

indeed of any object, are in a continual state of rapid jumping movement. It was soon clear that this motion was not due to living matter, but was common to all small grains, and it has been since known as " Brownian motion."

It can be easily seen with a magnification of about 500 to 800 diameters ; and the granules of ordinary water-colour paints are suitable objects. The motion is quite irregular ; a particle makes a hop in one direction, stops for an instant, and then jumps in another direction ; the distance traversed in each jump is quite arbitrary, but after a little observation it soon becomes evident that it is the smaller and lighter particles which jump fastest and farthest ; thus, particles of the light gamboge are much more active than those of the heavy vermilion.

This motion is unceasing ; it is not affected by light, nor by small variations of temperature. It is also persistent in liquids other than water ; but it is stopped by addition of an electrolyte to the liquid ; different electrolytes, however, have different powers of causing settling. Settling is accompanied by the particles cohering to larger masses or flocks ; they then settle slowly, and stop their jumping motion.

The motion of the particles can be directed, to some extent ; if an electric strain of 8 or 10 volts is kept up in the liquid, by immersing in it two wires forming the negative and positive terminals

of a battery, the particles move either from the positive to the negative pole, or from the negative to the positive, according to their nature ; some substances appear to be positively, others negatively electrified.

Similar motion takes place in the dust particles in air ; the " dancing of motes in the sunbeam " is due to the jumping motion of every minute particle ; it must not be confused, however, with motion due to air currents, which carries streams of particles in one direction. If ordinary tobacco smoke be blown into a small flat chamber forming the slide of a microscope, this motion can be seen ; it resembles the flight of minute butterflies ; they are now more, now less distinct, according as they come into focus, or dance up or down.

It has recently been shown that the motion is due to the impacts of the molecules of the liquid on these microscopic grains ; this explanation was suggested in 1863 by Wiener ; in 1876 the same suggestion was brought forward by Ramsay ; and it was defended by Gouy in 1888 ; but no satisfactory evidence was brought forward at that time to settle the cause of the Brownian motion.

Now, however, owing to the brilliant experiments of Jean Perrin and others, and to the advance in our knowledge of the dimensions of invisible molecules, the same results as hold for molecules can be visually demonstrated for visible particles.

The diameters of such visible particles can be measured by using a microscope furnished with a micrometer scale ; that is not possible for actual molecules ; but in order to compare the small with the large, it is necessary to know the approximate size of real molecules.   This can be determined.

We saw, towards the end of last chapter, that it is obvious that molecules must collide at their surfaces, and not at their centres ; consequently Boyle's Law, that the volume diminishes in proportion as the pressure of a gas rises, cannot be rigorously true.   Suppose 100 volumes of a gas at, say, the pressure of the atmosphere ; according to Boyle's Law, at a pressure of two atmospheres, the volume of the gas should become 50.   But suppose that the hundred volumes of gas consist of 99 volumes of " space," and one volume filled by the " solid " molecules ; then, on the assumption that the molecules themselves are incompressible, the 99 volumes should become, when the pressure is doubled, 49·5 volumes ; and adding the one volume filled by the molecules, the ultimate volume of the gas would be, not 50 volumes, but $49·5+1=50·5$ volumes.

From this it can be seen that by careful measurments of the compressibility of a gas, so as to determine the deviation from Boyle's Law, it should be possible to calculate the space " occupied" by the molecules, as compared with that "inhabited " by them.

VISIBLE "MOLECULES"

Another way of solving the same problem has been arrived at by the Dutch physicist Van der Waals, which leads to the conclusion that the volume of the molecules is approximately one-third of the volume of the liquid ; or,

$$n \times \text{volume of } 1 \text{ molecule} = \tfrac{1}{3} \text{ volume of liquid,}$$
where n =number of molecules.

Evidently, the volume which the molecules occupy in the state of gas will not, on the reasonable assumption that they are incompressible, differ from that which they occupy in the state of liquid, although the volume *inhabited* by them is very much larger. If, then, we were to add to our knowledge of the actual volume occupied by the molecules of a gas, a knowledge of the *average free path* of a molecule, that is, the average distance which a molecule traverses between collisions with its neighbours, the length of the free path will be diminished, as already stated on page 94, by the diameter of a molecule ; and that magnitude can thus be arrived at. We must therefore consider how the free path is measured.

A gas, like all other forms of matter, can be made to undergo friction. This is easily shown by allowing coal gas to pass through a narrow tube, and lighting it at the far end. With a certain pressure of gas, and length of tube, a flame of a certain length will be seen. By using a longer tube of the same bore, there is more friction in

passing, and less gas issues, and consequently the flame is a smaller one. We can realize what happens here by a simple analogy. The molecules of gas, it must be remembered, are in very rapid motion. The layer of gas next the wall of the tube may be regarded as comparatively stationary, so that the gas passing down the middle of the tube is interchanging molecules with the stationary layer. It is as if two trains were moving parallel to each other, but with different velocities ; and that it were possible for the passengers in each to jump on to the other, while the trains are moving. It is clear that the passengers on the quickly moving train will, as it were, convey their motion to the slowly moving train, and slightly accelerate it ; and similarly, those which jump from the slow to the fast train will slightly retard the latter. The influence which the one set of molecules has on the other measures the *viscosity* of the gas. Clausius showed that the relation of the viscosity to other properties of the gas can be represented thus :—

Viscosity $=\frac{1}{3}$ density $\times$ free path $\times$ average velocity of the molecules.

The density and the viscosity can be measured, and we have already seen (p. 91) how it is possible to calculate the average velocity. That for oxygen, for example, calculated by the same process as already explained, gives to a molecule the velocity on the average of 500 metres per second at the

ordinary temperature. The pressure, it will be remembered, is $=\frac{1}{3}$ density × square of molecular velocity. Here, pressure and density can be measured, and the average velocity of a molecule follows.

The figures thus obtained for oxygen are :—

1. Free path $=0.964 \times 10^{-4}$ millimetres, or about the tenth of a micron.

2. Molecule's diameter $=61 \times 10^{-8}$ millimetre ; or, if one and a half millions of them were placed in a row, it would be about a millimetre long.

3. Number of molecules per cubic centimetre $= 2.7 \times 10^{19}$. As a cubic centimetre of oxygen weighs nearly 1.4 milligram, a molecule of oxygen must weigh $\dfrac{1.4 \text{ mgr.}}{2.7 \times 10^{19}}$, or $0.52/10^{19}$ milligram ; and as a molecule of oxygen consists of two atoms, an atom of oxygen must weigh 2.6×10^{-20} milligram. As, according to Avogadro's Law, equal volumes of gases contain equal numbers of molecules, we can calculate from these data the weight of any molecule of which we know the weight relative to that of oxygen.

Avogadro's Law can be stated in a somewhat different fashion, namely, equal numbers of molecules of different gases, occupying equal volumes at the same temperature, exert equal pressures on the walls of the vessel containing them. We have seen, moreover (p. 21), that, according to Boyle's Law, the pressure of a gas

varies inversely as its volume, temperature being kept constant. We have also learned that these laws have been extended by van't Hoff to dilute solutions (p. 34). Of course, by pressure in the case of liquids, osmotic pressure is understood ; that is, the pressure due to the dissolved substance. These laws, be it remarked, apply to molecules of very different complexity, and consequently of very different weight ; they apply as well to an ion of hydrogen of practically the same weight as an atom, as to a molecule of albumen, of which the molecular weight is several thousand times as great. The question may be raised : Do these laws not also apply to particles in Brownian motion ?

Linder and Picton, in 1897, showed that what are generally called " colloidal solutions," that is, somewhat opalescent liquids containing bodies generally taken to be insoluble in water, are really suspensions of fine particles, which may be seen under high magnification to be particles in very rapid Brownian motion. If such a solution be subjected to an electric strain, as already mentioned, the particles are sometimes made to move to the positive, sometimes to the negative pole, according to their nature. Ramsay and Senter found that a solution of sulphide of arsenic of this nature has the same density, whether it be measured by actually weighing a known volume, or by a hydrometer. It may be explained that the

flotation of any body must in the last instance be due to the molecular bombardments which it undergoes. Now, if the particles of arsenious sulphide can so bombard the hydrometer as to make the density determined by its aid identical with that obtained by weighing, then it would follow that such particles act in this respect as molecules, and behave as the kinetic theory of gases would suggest. It was found that this anticipation was fulfilled ; the particles actually exert pressure, due to their mass and their motion, as if they were enormous molecules.

The complete analogy of such visible particles with molecules has been lately proved in a beautiful series of experiments by Jean Perrin, of the University of Paris. The pressure exerted by a number of molecules, it will be remembered, is dependent (1) on the number of molecules in unit volume ; (2) on the mass of each molecule ; and if all the molecules are of the same kind, the mass of each will be the same ; and (3) on the square of the velocity with which the molecule moves, on the average. In symbols, $p = \frac{1}{3}nmC^2/v$, n being number, m mass, C velocity, and v volume ; if volume be taken as unity, then it need not be considered in the equation.

Everyone knows that the air is more rarefied on the top of a mountain than at sea-level; and, indeed, this gives a well-known method of finding the height of a mountain ; the height of the

barometer on the top is compared with that at the bottom ; and knowing the law of rarefaction, first indicated by Laplace, that a rise of about 6 kilometres reduces the density of the air to half, no matter at what height the start may be made, the altitude can be calculated. But this figure, 6 kilometres, obviously applies only to air ; for a lighter gas, such as hydrogen, the rise would need to be much greater to halve its pressure ; and less if the atmosphere consisted of a heavier gas, such as carbon dioxide. It is easy to see that the heights which would entail the same lessening of pressure, or, what is the same thing, the same fall of the barometer (always provided that the temperature is constant), must be inversely proportional to the densities, and consequently to the molecular weights of the gases of which the atmosphere consists. For instance, if it were necessary to rise 5 kilometres in an atmosphere of oxygen at $0°C.$, before its density were halved, it would be necessary to rise no less than 80 kilometres in hydrogen at $0°$, because the density of hydrogen is only one-sixteenth of that of oxygen. Now, if the density be halved, it is because the same volume of the gas contains only half the number of molecules. And as the pressure is due to the impacts of the molecules, the pressure of the gas will also be halved. As it is always better to visualize such phenomena, the accompanying figure will give an idea of the state of affairs in three tubes, of which number 1,

the longest, is about 300 kilometres high ; the
molecules of gas are much more numerous below
than higher up ; the left-hand tube is supposed
to contain hydrogen, the middle tube helium, and
the right-hand tube oxygen.
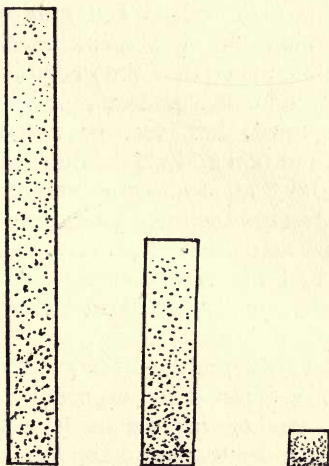
Fig. 2

On the assumption that the distribution of the
particles in a liquid should be similar to that in a
gas, if the particles are uniform in size, they can
be examined. But from data which have already
been given, it is possible to estimate the height

at which the density of distribution of the particles should be halved ; it is about the twentieth of a millimetre, or 100 million times smaller than the height at which the density of distribution or, what is the same thing, the pressure of oxygen would be halved. If these figures are correct, it would follow that each particle weighs 100 million times as much as a molecule of oxygen. And supposing it were possible to arrive at the weight of a particle, the actual weight of a molecule of oxygen would follow. It must, however, be noted that the effective weight of a grain is the difference between its weight and that of an equal volume of water ; for that represents the force pulling it downwards, owing to the attraction of gravity. Of course, if the grains had the same density as water, they would remain equally distributed throughout the liquid.

Monsieur Perrin prepared the grains which lent themselves best for this purpose by pouring a solution of gamboge or mastic (a sort of resin) into water. Under the microscope, the precipitate is seen to consist of round granules, but of different sizes ; they are hard, and not sticky. To sort them into lots of uniform size, centrifugalizing was resorted to ; the suspension was placed in a long tube, forming the radius of a whirling-table, which was rapidly revolved. The larger grains, under the action of centrifugal force, settle more quickly than the smaller grains, because the surface

of a large grain, being smaller relatively to its mass than the surface of a small grain, suffers proportionally less friction with the water during settling. It is for the same reason that a feather sinks slowly in air, while a shot drops with hardly any retardation from the friction of the atmosphere. Fractions of the turbid liquid were removed, and the operation repeated and repeated, for several months, until a suspension was obtained in which all the granules had nearly the same diameter.

It was then necessary to determine the density of the gamboge ; this is not difficult ; the weight of the suspension in a flask was determined, and the total weight of the resin was arrived at by evaporating the water and weighing the dry residue. But to know the weight of a grain, their diameter had to be found, and this is not so easy, for they were so small that a direct measurement of the diameter was attended by an error of 20 per cent. An approximate result was arrived at, however, by evaporating a droplet on a microscope slide ; the liquid dries up, leaving the grains pretty evenly distributed, and in apparent contact with each other, so that the number lying in a row, the length of which can be measured, can be counted ; the diameter of one grain is found by dividing the length by the number of grains in the row.

Another plan which gave better results was to place a measured volume of the suspension in a

cylindrical glass with a flat bottom ; it was observed that if the suspension was made slightly acid, the grains adhered to the surface ; and after all the grains had stuck, those which adhered to the bottom were counted. A third method was to determine the time necessary for the suspension to clear, when placed in a cylindrical tube some centimetres long ; the law discovered by Stokes, relating to the fall of a sphere in a viscous fluid, was then applied, and as that involves the diameter of a grain, it was thus estimated. All three methods gave concordant results. The best measurements were obtained with grains having a diameter of 0·212 micron, i.e. a little more than the 5000th of a millimetre. The density of the gamboge was found to be, in the state of emulsion, 1·206.

The vessel containing the emulsion was a disc-shaped depression in a microscope slide, about a millimetre in depth. A drop of the emulsion was placed in this little trough, and it was immediately covered with a cover-glass, which, to prevent evaporation, was paraffined at the edge. After standing for three hours, the grains, which are at first uniformly scattered through the liquid, have reached a steady state, which is not altered after 15 days, and would certainly be permanent. The actual method of making the observations was to focus a microscope on a point 5 microns from the bottom of the little trough, then on a point 35

microns higher up, then 65 microns, and lastly 95 microns. At each of these positions a photograph of the particles in focus was instantaneously taken, and the number of grains in a given area was counted. This was a work of some magnitude ; for instance, on one occasion the number counted was 13,000, and the relative numbers at each depth, taking that of 5 microns from the bottom of the trough as 100, were : 100, 47, 22·6, and 12 ; these numbers are practically the same as 100, 48, 23, and 11·1, which are exactly in geometrical progression. It is seen that each rise of 30 microns in height lowers the concentration of the granules to about half the previous value. For other grains of greater size a rise of 6 microns halved the concentration of the granules. Numerous observations of the kind were made, with grains of varying size, and always with proportional results ; the height of half-concentration varied inversely with the relative weights of the particles, as is the case with gases.

Avogadro's Law, which is that at equal temperatures and at equal pressures equal volumes of gases contain equal numbers of molecules, may be stated thus : The molecular weight of any gas expressed in grams occupies the same volume as that occupied by 2 grams of hydrogen, viz. 22,380 cubic centimetres ; and this is equivalent to the statement : all gram-molecules contain the same number of molecules. Thus, there is the same

number of molecules in 2·016 grams of hydrogen
as in 32 grams of oxygen, 18·016 grams of water-
vapour, 28·02 grams of nitrogen, etc., provided
the gases have been measured at the same pressure
and temperature. This number, N, may be
termed Avogadro's constant.

The mean of five series of measurements made
by Perrin gave to N the value 69×10^{22}; a sixth
series, made with the utmost precaution, made
N $70·5 \times 10^{22}$, and this number is taken by him as
final. As that is the number of molecules in
22,380 cubic centimetres, the number in one cubic
centimetre is 70·5/22,380, or $3·15 \times 10^{19}$. This
conclusion has, however, been modified by the
American physicist Millikan, who has kept a
droplet of oil of known diameter floating in air by
opposing an electric strain to the action of gravity;
this droplet picks up electrons, and the diminution
of charge necessary to keep the droplet stationary
has been measured. The number 60·63 is thus
substituted for Perrin's figure 70·5.

From that datum it is possible to calculate the
mass of any atom; for example, that of an atom
of oxygen is 32/N, or $52·8 \times 10^{-24}$ gram, for a
molecule; and as a molecule of oxygen contains
two atoms, an atom weighs $26·4 \times 10^{-24}$ gram.
That of an atom of hydrogen is 1·008/N, or $1·63 \times 10^{-24}$ gram; and as we shall learn in the next
chapter that there exist masses much more minute
than atoms, to which the name " corpuscles " has

been given, we may anticipate by stating that the mass of a corpuscle is 1830 times less than that of an atom of hydrogen, or 0.8×10^{-27} gram.

The molecular diameters of some gaseous elements are given in the following table, which is taken from the memoir published by Perrin in the *Annales de Chimie et de Physique* :—

Helium	1.7×10^{-8}	centimetre
Argon	2.7×10^{-8}	,,
Mercury	2.8×10^{-8}	,,
Hydrogen	2.0×10^{-8}	,,
Oxygen	2.6×10^{-8}	,,
Nitrogen	2.7×10^{-8}	,,
Chlorine	4.0×10^{-8}	,,

CHAPTER VIII

ELECTRONS

IN 1879, Mr. (now Sir) William Crookes communicated a paper to the Royal Society, entitled "Molecular Physics in High Vacua." In it he showed that if a glass tube be constructed so that an electric discharge can be passed through it from a wire sealed through each end, and if the glass tube be exhausted of air to a great extent, there is seen on the glass near the negative pole a green colour, due to phosphorescence. If the negative pole be a plate of metal, " rays " appear to be propelled normally to the plate ; and the glass shows green phosphorescence round the positive pole, where the rays appear to impinge. Even if the positive pole be placed elsewhere, the rays follow a straight path, at right angles to the negative plate. By making the negative plate a cup, the rays can be concentrated to a point ; and any object placed at that point becomes intensely hot. By interposing a cross cut out of lead or any other metal between the negative plate and the opposite end of the tube, a shadow is cast ; whereas the glass glows with a brilliant green colour where

not protected from the incident rays, the shadow of the cross makes a dark patch.

It was Crookes's view that the "rays" consist of a stream of electrified molecules of residual gas, for even though a "vacuous tube" is comparatively free from molecules of oxygen and nitrogen, still the word "vacuous" is only a relative term ; and even in a "high vacuum" there are many molecules left, which the best pump fails to extract. That these projected molecules do not consist of the material of the negative electrode "splashed off" was shown by constructing it of platinum ; although platinum gives a deposit in the neighbourhood of the electrode, no deposit is formed after long exposure of the tube to the rays, accompanied by bright phosphorescence all the time. Hence he attributed the luminosity of the glass to its bombardment by molecules of the constituents of air, the residual gas in the tube.

To determine whether or no these rays consisted of electrified molecules, he constructed an apparatus in which the rays, after leaving the negative plate, passed through two slits in a plate of aluminium ; the result was two parallel rays, invisible, of course, until they impinged on the glass tube at the opposite end. To render them visible, the rays were caused to graze a screen of mica, painted over with a phosphorescent powder ; in this way the course of the rays could be traced.

These rays diverged. The experiment was varied, so that each ray started from its own plate ; and either plate could at will be made the negative pole. The plates were so arranged that the rays from each, when excited alone, fell on a point at the opposite end of the tube; when both plates were made negative, the rays, instead of converging, were parallel to each other, showing that there was repulsion between them. They behave, in fact, like adjacent streams of similarly electrified bodies, and the conclusion was inevitable, that they consisted of such.

From these observations Crookes named these rays "a fourth state of matter," as opposed to the three previously known states, the solid, the liquid, and the gaseous.

In 1888, it occurred to Lenard, then assistant to Professor Quincke in Heidelberg, that if the rays investigated by Crookes could be caused to pass through a diaphragm, it would show whether they consisted, like light, of undulations in the ether, as was supposed by Professor Wiedemann, or whether, according to the hypothesis of Crookes, they were in reality particles of matter or molecules shot off from the negative pole. He made an apparatus like that of Crookes, but furnished it with a window of very thin quartz ; quartz is transparent to rays of ultraviolet light, and he imagined that it would more readily allow the "cathode rays," as the rays discovered by Crookes

came to be called, to pass through. But no effect could be detected ; on the further side of the quartz window, neither phosphorescence was to be found, nor were any electrical phenomena noticeable.

Four years later, in 1892, when Lenard had become the assistant of Professor Hertz, of Bonn, his chief discovered that thin plates of metal are transparent to cathode rays. In these experiments he used very thin leaves of gold, silver, and aluminium, such as are employed by bookbinders. He showed Lenard an experiment in which a piece of uranium glass, which has the power of phosphorescing under the influence of cathode rays, was covered with a piece of aluminium leaf, and exposed to Crookes's rays inside a vacuum-tube ; even where the aluminium covered the glass, the glass still phosphoresced, showing that the rays could pass through the aluminium. Lenard attempted to strengthen the aluminium leaf by superposing several thicknesses, and noted hardly any difference in the intensity of the phosphorescence produced by cathode rays impinging on the thicker leaf. He then made use of his old apparatus with the quartz window, and fitted it up with a stout metal plate, instead of the quartz one ; this plate had a small hole in the middle, on which a thin plate of aluminium foil—not leaf, which is much thinner—was fastened airtight ; this plate closed the end of his vacuum-tube ; and

when cathode rays were made to impinge on the aluminium window, some rays passed through ; and it transpired that they could penetrate considerable thicknesses of air before losing their power to excite phosphorescence. They also impressed themselves on a photographic plate. These, however, are the properties of ultraviolet light. But for such rays, air is by no means so transparent as it is for light ; they become scattered, and at less than four inches the thickness of the layer of air extinguishes them. Indeed, the appearance may be likened to that of light passing through a layer of water to which a little milk has been added ; and in this case it is the globules of fat in the milk, which are opaque to light, which prevent the light from passing. The molecules of air, which oppose the passage of the cathode rays, are at least, as we have seen, ten thousand times as small as the milk-globules ; indeed, they are so small as to make it impossible that what they stop can be anything of the nature of light ; the cathode rays must consist of minute particles, commensurate in size with the molecules of the constituents of the air which stops their passage.

Measurements made it clear that the stoppage of the cathode rays was proportional to the density of the material of the screen ; a screen of gold, which is about ten times as dense as aluminium, has, if equally thick, ten times the stopping power

of a screen of aluminium. The nature of the material of the screen was without influence on the absorption; only its thickness and its density.

As long ago as 1869, Hittorf had noticed that such rays are deviable by a magnet; and in 1876, Goldstein had made a similar discovery for the rays, if placed in an electric field. Both the magnetic and electric deflections are explicable on the assumption that the " rays " are really streams of negatively electrified particles; and as we shall see later, it is possible by measurements of the amount of such deflection, to arrive at an estimate of the velocity of the supposed masses, and also of the ratio between the electric charge and the mass of each particle. Rough measurements of this nature showed that supposing the particles to consist of hydrogen, the charge carried by each particle would be about 1000 times as great as the charge carried by an atom of hydrogen. Assuming the charge carried by a particle to be equal to that carried by an atom of hydrogen during electrolysis, it would follow that the mass of the particle carrying the charge would be only one-thousandth of that of an atom of hydrogen. But such particles cannot be material, in the ordinary sense of the word; and Lenard began to suspect that the particles consisted of *electricity itself*. For the first time electricity had been recognized, not in conjunction with matter. In

fact, the travelling particles were the *electrons*, so named by Dr. Johnstone Stoney, as already mentioned on page 51.

It has been mentioned that these streams of particles or " corpuscles " can be deviated by a magnet at right angles to the direction of the magnetic force, and also at right angles to the direction in which the rays are moving. Supposing that the particles are moving horizontally from east to west, and the magnetic force is horizontal from north to south, then the particles will be deflected downwards. That the particles convey negative electricity was first proved by Perrin ; they were deflected by a magnet, so that they impinged on an electrometer, which then acquired a negative charge. Sir J. J. Thomson, in his turn, found that they could be equally well deflected by an electrified body ; this confirmed and completed the experiment made by Crookes, when he showed that two streams of the particles repel each other. Thomson made this a means of determining the velocity of the particles, in the following way : the amount of magnetic deflection is proportional, as indeed appears reasonable, to the magnitude of the charge, to the velocity with which the particle is moving, and lastly, to the intensity of the magnetic force. An electric field will also deflect the particle ; but in this case the amount of deflection bears no relation to the velocity with which the particle is moving

it is proportional solely to the intensity of the electric field, and to the magnitude of the charge on the particle. Suppose an apparatus to be constructed which allows of the stream of particles to be acted on simultaneously by magnetic and by electric forces, but so arranged that the two oppose each other, the strength of the two fields can be so balanced that the particles are not deflected, but pursue a straight path ; this, of course, can easily be detected by the device of causing the particles to strike a phosphorescent screen ; if the patch of green light remains stationary, there is no deflection. In this case the forces are balanced. We therefore have—Magnetic force, H × charge, e × velocity of particle, v = Electric force, X × Charge, e. Eliminating e, we have—Velocity, v = Force of electric field, X, divided by magnetic force, H. Now, the force of the electric field and the magnetic force can be both measured ; and the velocity of a moving particle can be deduced. It depends on the exhaustion of the tube in which the stream of particles flows ; in a highly exhausted tube it may be 60,000 miles a second ; in less well-exhausted tubes it may not exceed 5000 miles a second ; in all cases, the velocity is much greater than that of any body known ; the higher velocities compare with that of light, which is 180,000 miles a second.

The next problem which Thomson solved was the determination of the ratio of the charge on a

particle to its mass. The importance of this knowledge can be realized by reference to page 49. Faraday's Law is there quoted ; it is : when compounds are decomposed by the same electric current, the relative weights of the ions discharged, and therefore set free, are proportional to the equivalents of these ions. Thus, the same charge is carried by an atom of hydrogen, of which the weight is taken as unity, as by an atom of sodium, of which the atomic weight is 23, or of chlorine, of atomic weight 35·5, and so on. Dyad atoms carry two, triad atoms three charges, and so on. When carrying these charges, they are termed " ions." Now, corpuscles, or particles which are shot out from the negative pole, and which in mass form cathode rays, must almost certainly carry a small number of charges, probably one each ; and by assuming what is exceedingly probable, that the charge is of the same magnitude as that carried by a monovalent ion, then, if the ratio between the charge and the mass which carries it is known, it follows that the mass of the corpuscle can be found by a very simple calculation. Hence the importance of determining the ratio of the charge to the mass.

This ratio can be found by acting on the rays by an electric field alone, and the problem then resembles that of a bullet being acted on by gravity, and falling during its path. The farther it falls, the quicker it falls, because the force of

gravity is continually accelerating its rate of motion. The same is true of the corpuscle ; the electric force pulls it out of its path, and it is obvious that the acceleration will be proportional to the strength of the electric field, which has been given the symbol X ; it will also be proportional to the amount of the charge, e ; and as the smaller the mass, the more rapidly it will be accelerated, the acceleration will be inversely proportional to the mass. In symbols, Acceleration $= Xe/m$. Returning for a moment to the bullet, the distance which it will fall is equal to $\frac{1}{2}gt^2$, where g is the force of gravity, and t is time. Similarly, the displacement of the patch of luminescence on the screen, caused by the deviation of the cathode rays by the electric field, which corresponds to the fall of the bullet, will be equal to $\frac{1}{2}Xe/m \times t^2$. Now, velocity is distance divided by time, or l/t ; and consequently, time is distance divided by velocity, or l/v ; and $t^2 = l^2/v^2$; hence by measuring the length of the path of the rays, and knowing the velocity, determined as already described, the value of l^2/v^2 is known. And the displacement, which we shall term d, can be measured on the screen. As $d = \frac{1}{2}Xe/m \times l^2/v^2$, $e/m = 2d/X \times v^2/l^2$; all the terms on the right hand of the equation can be found by measurement.

On carrying out experiments to find this ratio, by deflecting cathode rays by an electric field, Thomson found that whatever gas had been in

his tube, and whatever the velocity of the cathode stream, the same value for e/m was always found ; the charge always bore the same ratio to the mass. The value of this constant ratio, expressed in the " centimetre-gram-second " system of electrostatic units, is 5.31×10^{17} units. This is the greatest known value for this magnitude ; an ion of hydrogen carries a charge, and the ratio of e/m for hydrogen, which, until the investigation of the cathode rays had been the highest known, is 2.90×10^{14} ; the ratio is 1.83×10^3, or 1 to 1830. Either, then, the charge is 1830 times that carried by an atom of hydrogen, or the mass of the particle is only the 1830th of that of an atom of hydrogen.

That the latter is the correct conclusion was proved by actually measuring the value of e, the charge, using a method devised by C. T. R. Wilson. It was long ago discovered by John Aitken that fogs are caused by particles of dust acting as nuclei for the condensation of the water vapour in the atmosphere. Each particle of dust collects round it a droplet of water, and the droplets form a mist. Now, if the air be cooled, the water-vapour may separate, provided there is anything for it to condense on ; if not, the air is said to be " supersaturated " ; it retains more moisture than ought normally to be there. Introduce a little dusty air, and an immediate fog is produced. When air is compressed it becomes hot, as every-one knows who has used a bicycle-pump ; con-

versely, if allowed to expand, it becomes colder, and by controlling the amount of expansion the amount of cooling can be regulated. Wilson showed that if no dust whatever be present in the air (and this can be contrived by filtering the air through cotton-wool, which retains all the dust-particles), the air can be cooled to such an extent that it contains no less than eight times the moisture in the state of gas than what it should normally contain. If it be further cooled, then the moisture suddenly separates as a miniature shower of rain. Wilson also found that when the air contains charged particles, then condensation will take place at a temperature corresponding to a fourfold, instead of an eightfold saturation. This was carried out in practice by confining the air in a chamber of glass, closed by a piston. The cooling of the air is greater, if it is more expanded ; this is achieved by causing the piston to fall to a greater or less distance. If the air is made to expand, so that the supersaturation is more than fourfold and less than eightfold the normal, then if no dust is present, no fog will be formed on expansion. If the gas is now brought into a conducting state (and this, for reasons shortly to be seen, is most easily managed by bringing a little radium near the vessel), expansion produces a cloud of particles ; and by regulating the amount of expansion, the actual weight of the water separated as a mist, in droplets, can be calculated.

That the condensation is actually produced by electrified particles is proved by having inside the vessel two metallic plates which are kept oppositely electrified ; the positive plate attracts the negative particles, and the negative plate the positive particles ; and on cooling the gas by expansion practically no cloud is formed. The electrified particles, which are always present in minute amount in ordinary air, have thus been removed.

Knowing the weight of the condensed water, if the volume of one of the drops were known, it is clear that the number of drops could be estimated ; and on the assumption that each drop carries one electron, or one unit charge, the number of corpuscles could be arrived at. These droplets fall ; and although a falling body of any visible size accelerates its rate of motion during its fall, if the falling body is very small its surface is great in proportion to its mass ; and the friction of the air soon impedes the fall, so that the rate of fall, after an instant of time, becomes uniform ; a balance is set up between the force with which the earth attracts the falling particle and the opposing friction of the air. The law governing the fall of minute bodies has been stated by Sir George Stokes ; it is, that the velocity is directly proportional to the square of the radius of the drop (equivalent to its area), and to the acceleration caused by gravity, and inversely proportional to

the coefficient of viscosity of the air ; for the more " viscous " the medium, the greater the resistance to the fall. Giving the symbols v for the velocity of the fall, g for the acceleration due to gravity, r for the radius of the drop, and the Greek letter η for the coefficient of viscosity of the air, Stokes's Law is :—

$$v = 2/9 \times \frac{gr^2}{\eta} ;$$ and by substituting known values of g and η, $v = 1 \cdot 28 \times 10^6 \times r^2,$

so that if the velocity of the fall of the drop can be measured, its radius can be determined, and from the radius the volume can be calculated. In this way the number of corpuscles was arrived at ; and as the total quantity of electricity on the precipitated liquid is easily measured, the charge on each particle can be estimated.

If two small spheres of conducting material be so placed that their centres are exactly 1 centimetre apart ; and if each sphere be equally charged, say negatively, they will repel each other with a certain force which will be greater if the charges are greater, smaller for smaller charges. Suppose, now, that the charges are so adjusted that the repelling force is 1 dyne (see p. 12), then the quantity of electricity carried by each sphere is taken as unity, and is named an *electrostatic unit*.

It will be recalled (see p. 49) that Faraday

proved that equivalents of elements or groups of elements convey equal quantities of electricity. Now, $1 \cdot 008$ is the equivalent of hydrogen (for it is chosen as unity) ; and it has been shown by very accurate experiments that $1 \cdot 008$ gram of hydrogen, when set free by electrolysis, has conveyed $2 \cdot 9 \times 10^{14}$ positive electrostatic units. It is also known that 1 gram of hydrogen, measured at $0°C.$ and at a pressure of 760 millimetres of mercury, occupies 11,190 cubic centimetres, and that the number of molecules of hydrogen, or indeed of any other gas in that volume, is $30 \cdot 31 \times 10^{22}$ (Millikan ; see p. 110). But each of these molecules consists of two atoms ; hence a gram of hydrogen consists of $60 \cdot 63 \times 10^{22}$ atoms. Dividing $2 \cdot 9 \times 10^{14}$ by $60 \cdot 63 \times 10^{22}$, the quotient is $4 \cdot 78 \times 10^{-10}$; and this number is almost identical with that found by the American physicist Millikan, who has carried out most beautiful experiments according to methods originally devised by H. A. Wilson in Sir J. J. Thomson's laboratory ; he found the value $4 \cdot 777 \times 10^{-10}$ for the electric value of a unit charge, or an electron.

To sum up : cathode rays consist of streams of electrons or particles of negative electricity ; each electron is a charge of $4 \cdot 78 \times 10^{-10}$ electrostatic unit ; each atom of hydrogen deprived of an electron forms an ion ; it is " positively charged," and the charge which the atom loses on becoming an ion has the same value, viz. $4 \cdot 78 \times 10^{-10}$

electrostatic unit. And as the mass of an electron is known to be 1/1830th of that of an atom of hydrogen, and as the mass of an atom of hydrogen (see Perrin, p. 110) is 1.63×100^{-24} gram, that of the electron is 0.8×10^{-27} gram. It is the smallest mass of which we know the existence, but its combination with or loss by atoms of other elements profoundly modifies their properties.

CHAPTER IX

ELECTRONS AND MATTER

IF the reader will refer to p. 51, he will re-collect that electrons can attach themselves to matter ; in fact, they behave more or less as if they were chemical elements, forming compounds with the recognized elements, just as elements combine among themselves. Indeed, they appear to be essential constituents of all compounds, and probably of most, if not all, so-called elements.

For the elements themselves would appear to be only unusually stable compounds. The condition of their stability is their retaining their combined electrons ; to separate them from the constituent electrons requires the absorption of much energy, as a rule ; and when separated, the change results in what must be termed different forms of matter.

The discovery which has led to the acceptance of these views was made by the late Henri Becquerel, himself a distinguished physicist, and the son and grandson of men renowned in French science. In 1896, wishing to ascertain whether certain sub-stances can retain light, as a hot poker retains

heat, he exposed various salts to the rays of the sun, and laid them afterwards on a photographic plate wrapped up in black paper to protect it from ordinary light. Among these were salts of the metal uranium. The weather during a part of that year being too gloomy to allow of the exposure of the uranium salts to sunlight, he laid them aside in a drawer on the top of the plates. On developing the plates, he was surprised to find that where the uranium had lain, the plate was affected. Moreover, the uranium salt apparently retained this power without limit, even though it had been prepared in the dark, and never exposed to light. In the autumn of 1896, the author visited Becquerel's laboratory in company with Lord Kelvin and Sir George Stokes ; and these eminent physicists were at a loss to understand whence such a continuous supply of energy could come. Lord Kelvin leant to the supposition that the uranium served as a sort of trap to catch and transform radiant energy traversing space, so that, otherwise incapable of detection, it was so transformed as to produce chemical change.

Shortly after this discovery of Becquerel's, Madame Curie and her husband compared the effect on a photographic plate of the uranium salt with that of the mineral, pitchblende, from which the uranium compound is prepared ; and having remarked that the mineral, proportionately to the uranium which it contained, has a greater

action than the salt, Madame Curie separated the constituents of the pitchblende into compounds of the various metals which it contained. Pitchblende is a complex mineral, containing lead, copper, bismuth, iron, calcium, barium, and many other metals besides uranium. Monsieur Curie utilized a discovery of Becquerel's in order to test these various fractions ; this was that besides acting on a photographic plate, the " rays " from uranium were capable of discharging an electroscope, an instrument consisting of a pair of gold leaves, suspended from an insulating rod, and made to diverge by being charged electrically. Armed with an instrument by which the radiating power of the uranium could be measured quantitatively, Madame Curie discovered that of all the substances separated from the pitchblende, the fraction containing bismuth was the most " active " in discharging the electroscope ; she ascribed this power to its containing a hitherto undiscovered element, to which she gave the name " polonium." Shortly after, she announced the discovery of a still more active constituent of the residues of pitchblende containing barium ; this substance she named " radium." Another radioactive form of matter was also separated from the same mineral by Debierne, and almost simultaneously by Giesel ; it has received the name " actinium." Lastly, Schiff found that the element thorium, the oxide of which is the chief constituent of

the mantles of incandescent gas-lamps, likewise possesses the property of emitting radiations. It has since been shown by Hahn that the radio-activity of thorium is to be ascribed to its containing a trace of a body difficult to separate from it, to which the name "radiothorium" has been given.

Limits of space preclude the consideration of all these different forms of matter; only the general principles can be touched here; and as radium has for various reasons been much more closely investigated than any of the other radio-active forms of matter, it will be sufficient to describe it, and some of its derivatives.

Radium has been prepared in the state of metal by Madame Curie. It is white, hard, and at once attacked by water; it resembles barium and, to a less degree, calcium. Its salts, too, are similar to those of barium; the chloride and bromide resemble those of barium, and the sulphate, like that of barium, is insoluble. Its atomic weight has been determined by Madame Curie, by Ramsay and Whytlaw-Gray, and by Hönigschmid; all the determinations are in close accord, and place it at 226·4. Its spectrum has been mapped, and is generally like that of barium; in short, it possesses all the signs attributable to a genuine element.

But it has properties which, though perhaps also characteristic of elements, have not usually been attributed to them; it undergoes spontaneous

change. It slowly changes into helium, and into another gas, to which Rutherford and Soddy, its first investigators, gave the name " radium emanation." It had previously been noticed by Becquerel that salts of radium if left near any object rendered that object itself capable of discharging an electroscope ; and it was also observed that it was necessary that the radium should be in communication with the object through the air ; if shut up in a flask, it did not communicate this power to neighbouring materials. Rutherford and Soddy passed air through a solution of radium chloride, and found that the air, thus treated, discharged an electroscope ; but if passed on its way to the electroscope through a tube cooled by liquid air, this power left it, but the tube on warming up gave off a substance possessing the discharging power.

Ramsay and Soddy investigated the matter further, and discovered first, that on dissolving an old sample of radium chloride in water, small bubbles of a gas are evolved, which proved to be helium ; and second, that the so-called emanation is itself a gas, following the usual laws of compression, and of expansion on rise of temperature ; moreover, that if confined in a spectrum tube, it shows its own characteristic spectrum for a few minutes ; but on standing, this spectrum disappears, and is replaced gradually by that of helium.

Later, Ramsay and Whytlaw-Gray liquefied the gas, and measured its vapour-pressures at different temperatures ; they determined the freezing-point of the solid ; Watson mapped its spectrum accurately ; and lastly, by means of a " micro-balance," capable of estimating a difference of weight of the order of the millionth of a milligram, Ramsay and Whytlaw-Gray determined the weight of a known volume, and from this deduced its atomic weight. It is the last member of the inactive series of gases, of which the others are helium, neon, argon, krypton, and xenon ; its atomic weight is 222·4, differing from that of radium by four units, the weight of an atom of helium. Hence it would appear that radium splits into helium, and this gas, now known by the name " niton."

Becquerel showed that radium continually sends off three different kinds of " rays." The word ray was first employed in such a connection by Sir Isaac Newton, in discoursing on light. It may denote a succession of waves, as with light ; or it may mean a stream of particles ; Newton supposed that light was due to such a stream, but that view is not now held. The rays from radium were termed by Becquerel alpha, beta, and gamma, from the first three letters of the Greek alphabet. The alpha-rays are positively charged ; and their velocity, measured as described on p. 119, is about 20,000 kilometres per second, or about one-four-

teenth of that of light. The velocity, however, depends on the source of the rays. These rays cannot permeate vessels of ordinary glass ; but if the walls of the tube containing the substance from which they are projected are very thin, some of them pass through. Rutherford has succeeded in showing that the matter of which these rays consist is helium, one of the products of ths decomposition of niton. What is more, he has succeeded in counting the number of particlee expelled from a known weight of radium in a given time, by an exceedingly ingenious device. These rays, when they pass through air, ionize some of the atoms of oxygen and nitrogen ; the air therefore becomes a better conductor. A known (but very minute) quantity of radium was placed on the end of a glass rod, closing one end of a long tube ; alpha-particles were shot along the tube, passing between two oppositely charged plates, in which the charge was kept so high that a discharge between them was nearly able to take place. When each particle passes between the plates, a discharge takes place, and the number of discharges in a given time can be counted. Another method which has given similar results depends on a discovery made by Sir William Crookes, namely that alpha-particles, when they strike a screen of the phosphorescing material, zinc sulphide, produce as many flashes as there are particles ; by counting the number of flashes, therefore, the number of

particles can be estimated. The number of particles coincides with the number of atoms of helium evolved from the quantity of radium employed. It must now be explained how that number can be calculated.

Niton, the emanation from radium, when left to itself, decomposes and yields other products, to which the names "radium A," "radium B," "radium C," etc., have been given by Rutherford and Soddy. These are solid bodies ; some of their properties have been investigated ; but it must be remembered that on account of the extremely minute quantity in which they occur, they are quite invisible, and can be traced only by their power of discharging an electroscope. Now, if a sample of air containing niton be left in a vessel from which portions can be withdrawn, the niton will gradually change into these solid products, which deposit on the walls of the vessel. Supposing that the discharging power of the air containing the niton be measured immediately before introducing it into the storage vessel ; then if a sample of equal volume be transferred to an electroscope and its discharging power measured after 3·86 days, it will be found to be only one half of that of the original niton. This space of time is termed the " half life period " of niton. Similarly, a measurement carried out after the niton has been left for another interval of 3·86 days shows that the discharging power is only one quarter of what it

was originally ; after a third period, one-eighth, and so on. Mapping these times against the discharging powers, a curve results, of the form known as exponential ; it is clear that the amount will never be zero, but will approximate more and more nearly to zero, the longer the time. Although, therefore, the life of niton is theoretically infinite, it is possible to say definitely that its " half life period " is 3·86 days. What is the half life period of radium ?

That has been determined in the following manner. The volume of niton obtainable from a known weight of radium has been measured by Rutherford, by Debierne, and by Ramsay and Whytlaw-Gray, as well as by others, and it was found that from one gram of radium, the maximum amount of emanation which is obtainable is 0·6 cubic millimetre. The niton can never increase beyond this volume, because as it is produced it changes into solid products ; the radium produces niton, and the niton decomposes, so that there is equilibrium between one gram of radium and 0·6 cubic millimetre of niton, the weight of which is $6·07 \times 10^{-6}$ gram, or about six thousandths of a milligram. From the known rate of change of niton, it is possible to calculate the proportion of the total amount which undergoes change in each second ; this is termed the " radioactive constant " of the niton, and it has been proposed to designate it by the Greek letter corresponding to its name,

namely v (pronounced "nu"). The reciprocal of this quantity is the average life of the atom, $1/v$.

For niton, 1/482000th of the amount present changes per second; the average life of an atom is therefore 482,000 seconds, or 5·58 days, or in years, $15·3 \times 10^{-3}$ year. Niton is in balance with radium, when $6·07 \times 10^{-6}$ gram is in presence of 1 gram of radium; that is, as many atoms of niton as are being produced per second from the radium are disappearing from the niton. Hence, as

$6·07 \times 10^{-6}$	::	1	::	$15·3 \times 10^3$	::	x
Weight of niton		Weight of radium		Average life of niton		Average life of radium

And $15·3 \times 10^{-3}/6·07 \times 10^{-6} = 2520$ years. The amount of radium disappearing per year and changing into niton is 1/2520th of the whole. This gives the half life period of radium as about 1750 years; if one gram of radium were kept for that time, half of it would have become niton, and half would be left as radium.

Knowing, then, the weight of niton produced per second from a known weight of radium, knowing also the number of atoms in that weight of niton, and taking account of the fact that each atom of radium, in changing into niton, expels one alpha-particle, that is, one atom of helium, it is evident how that number can be compared with the number of flashes in a given time, due to the bombardment of the phosphorescent screen

by the rapidly moving atoms of helium. Comparison showed that that number is identical.

Were the intelligent inhabitant of some distant country, unacquainted with the blessings of modern civilization, to visit an artillery range, and to be stationed near the iron-plate target, he would probably infer, on seeing the flash of the discharge and the piercing of the target, that some missile produced the damage, even although he were quite unable to follow the flight of the projectile. The emission of alpha-particles from radium has been inferred from similar considerations. A beautiful experiment has, however, recently been carried out by Mr. C. T. R. Wilson, in which the particles leave their track in the medium through which they pass. Their path is as easily traced as that of a rocket on a dark night. Wilson's method of counting particles has already been described on p. 122 ; moist air, in a state of supersaturation, gives up its moisture to electrons, each electron serving as a nucleus, and forming a droplet. He has now, however, made each alpha-particle trace its path in condensed droplets by a device which shall now be described.

The "cloud-chamber" consists of a shallow circular box with a glass top, coated with gelatine ; moist gelatine is a conductor of electricity, so that an electric potential can be given to the glass top. The bottom of the box is a kind of piston, which can be suddenly depressed ; it is blackened, and

is also coated with a layer of gelatine. There was a potential of about 16 volts per centimetre between the top and the bottom of the box. This naturally cleared the contents of the box of any ions.
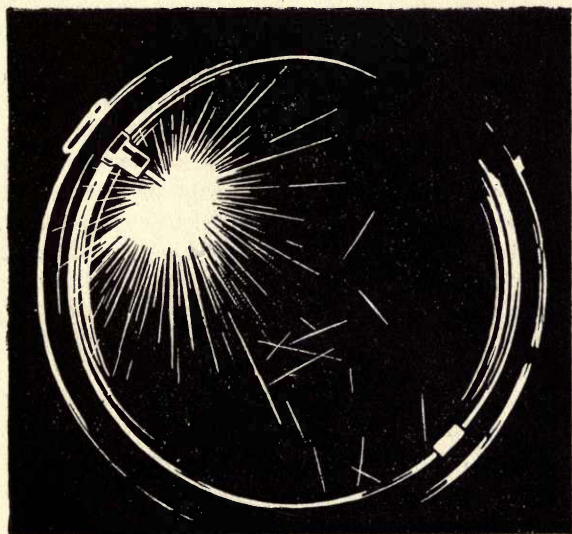
Fig. 3

A minute trace of a radium salt was placed at one side of the enclosed space; it is continually giving off electrons and helium, both kinds of particles moving with great velocity. A sudden

depression of the piston, that is, the bottom of the box, cools the air to such a temperature that moisture should deposit on particles of dust or on ions ; care is taken to exclude dust, by previously depositing all dust particles on the gelatine top and bottom of the box, by condensation of moisture. The ions alone are present, whether produced by alpha-particles or by electrons. With radium inside the box, the effect of a sudden expansion is to show a series of diverging straight lines, due to the moisture condensed by the ions produced in the air by the passage of both alpha and beta-particles ; these lines are surprisingly definite ; but almost at once they grow diffuse, owing to the diffusion of the droplets in all directions. By instantaneous illumination, made by an electric discharge an instant after the piston has been depressed, the paths of the rays remain on the eye, and the impression of their fading away by diffusion is avoided. There are also some tracks on the plate (Fig. 3) due to the expulsion of atoms of helium by some stray atoms of niton, given off from the radium.

To show the paths of the electrons, unaccompanied by helium atoms, the radium salt is placed outside the box, opposite a little window of thin aluminium, through which some of them can pass. Their track is represented by diverging straight lines of cloud condensation.

With X-rays, the nature of which is not yet

completely made out, the box shows minute streaks and patches of cloud ; it looks as if the effect of the X-rays is to liberate corpuscles, each endowed with energy sufficient to enable it to produce a large number of ions along its course.

Next to seeing these minute projectiles themselves is seeing their tracks ; and the onlooker who has once seen the demonstrations of Perrin and of Wilson cannot but acquire a deep conviction of the reality of the existence of both molecules and electrons, impossible to be conveyed by the somewhat abstract reasoning which first led to their adoption as constituents of matter.

CHAPTER X

TRANSMUTATION

THE word " transmutation " leads one back to the Middle Ages, to the times of the alchemists, when it was held that by help of the " Philosopher's stone " one form of matter could be converted into another. The reason for this superstition was doubtless the facts that a trace of dye could alter the appearance of a whole basket of wool, and also that the admixture of a trace of arsenic with copper changed its red colour to grey-white, and rendered it a brittle, hard metal instead of a soft and ductile one. These and similar phenomena gave the notion that chemical change of a fundamental nature could be brought about by the minute addition of foreign ingredients ; and, indeed, the idea is not a false one, for, although the transmutation of elements was for long regarded with scepticism, numerous cases are now known in which the physical properties of bodies are changed by the action of " catalytic " agents, which are themselves unaltered.

One of the greatest thinkers of last century, Michael Faraday, still held the hope that chemistry

would succeed in transmuting one element into another ; his words were : "To decompose the metals, to re-form them, and to realize the once absurd notion of transmutation—these are the problems now given to the chemist for solution." This hope has, in the opinion of the author, been realized.

A distinction must be drawn between "transmutation" and "transformation" ; the former may be understood to refer to a change accomplished by human agency ; the latter, to a change over which no control may be exercised. Beginning with the latter conception, it is evident that transformations are now well established. To explain the observations of Becquerel and the Curies, Rutherford and Soddy brought forward the theory that the radioactive elements are spontaneously changing into other, also elementary, forms of matter ; that their atoms are "disintegrating," or, as we should say if a compound were in question, are "decomposing." They based this theory originally on the fact that if the identity of a radioactive element can be established by the duration of its average life (and this appears to be a property as distinctive as any which serves to differentiate one form of matter from another) ; if, moreover, the quantity of an element which displays radioactive powers is proportional to its electric or photographic activity (and this admits of direct experimental verification), then there can

be no question that one form of matter changes into another different from itself.

The discovery of the salts of radium, and of its undoubtedly elementary character, lent additional force to their view ; and when Ramsay and Soddy actually separated niton or " radium emanation " in the state of gas, and when they discovered that in a closed tube containing niton it is slowly replaced by three times its volume of helium, the theory of disintegration or transformation was certainly established. The product of change of niton had been named by Rutherford and Soddy " radium A " ; when formed from niton, it was known that an alpha-particle was expelled ; it in its turn gave " radium B," but in this case merely beta-particles or electrons were lost ; the disintegration of " radium B " into " radium C " was again accompanied by the loss of an alpha-particle ; and lastly, the change of " radium C " into " radium D " also took place with escape of an alpha-particle. In all, three alpha-particles were lost. The transformation of " radium D " into other products need not be considered, for the rate is so slow (16 years) that the number of alpha-particles expelled during the time of observation would elude detection by measurement. The identity of alpha-particles, first regarded as an electrical phenomenon, with atoms of helium shows that from one volume of niton, if it be assumed to be a monatomic gas, three volumes of

helium, which is also monatomic, should be produced; and this has been proved, not only by measurement, but also by weighing. During the determination of the density of niton by Ramsay and Whytlaw-Gray, a tube containing a known weight of niton was left suspended on the microbalance for several months; it was then opened, the loss of weight determined, and that loss agreed with the weight of the three atoms of helium which had been removed with the pump, per atom of niton.

The definite properties of niton, its density, its vapour-pressures, its melting-point, its inactivity, its spectrum, all point to it being as well defined an element as those which are usually considered to be such; the same remark applies to helium, which has not been found to undergo any radioactive change; and from these two instances alone it might safely be concluded that the transformation of one element into another is an undoubted fact. But the case is strengthened by the discovery of helium as one of the disintegration products of thorium and of actinium; by the existence of long chains of bodies, apparently elementary, the result of the degradation of radium, of thorium, and of actinium; by the constancy in the proportion between the amount of uranium in its ores and the radium which is one of its products, due to a cause similar to that which renders the amount of niton constant, in presence of a definite weight of radium.

In short, the evidence for the instability of a number of elements is overwhelming.

The speculation naturally suggests itself—are all the elements unstable ? Is the special instability of the common elements not merely a matter of degree ? To these questions it is as yet impossible to give a rigorously definite answer ; but certain facts point towards the great probability of that answer being in the affirmative.

First, as regards the action of ultraviolet light, the disruptive effect of which on compounds admits of no denial. It has been known for long that if a polished plate of zinc, charged negatively, were exposed to vibrations of short wave-length in the invisible part of the spectrum, past the violet end, the plate would rapidly lose its charge. The same has been shown to happen with polished plates of a number of other elements ; and it has also been proved that the action of ultraviolet light causes the escape of material particles ; indeed, the surface of the plate becomes roughened. As yet, however, there is no proof that any transmutational change has occurred.

Second, the disintegration of the radioactive elements takes place with evolution of much heat. That evolved during the change into radium D of radium, passing through its various stages, is no less than 130 calories per gram of radium per hour ; that is, if a salt of radium containing one gram of radium metal were to transfer its heat

without loss to a gram of water, the water would be raised from 0° to 100° in an hour, and a small amount of the water would be evaporated besides. Ruthford has attempted to divide this heat among radium and its products. He ascribes 25 per cent of the total heat to the transformation of radium into niton ; 44 per cent to the change of niton and its first and second products, radium A and radium B, into radium C ; and 31 per cent to the disintegration of radium C. Radium D has a long life, and the amount of heat which it would liberate is distributed over such a long period of time, that it need not be considered.

Compounds which decompose with evolution of heat are said to be " endothermic," and they are always unstable ; for instance, " cordite," the explosive powder used for our artillery, evolves 1253 calories per gram with practically instantaneous suddenness ; the products are carbon dioxide, nitrogen, and water-vapour. Radium, yielding approximately 130 calories per hour, would in a year evolve about a million calories. As the half life period is 1750 years, it is possible to calculate the total quantity of heat which would be evolved, were all the gram to disintegrate ; it is $2 \cdot 8 \times 10^9$ calories ; but it would take a very long time ; it would be nearly complete after 20,000 years. The total energy evolved in the form of heat is more than two million times that given off during the explosion of an equal weight of cordite.

But that energy is due to the expulsion of only four alpha-particles: that evolved when radium changes into niton; that when niton turns into radium A; that when radium A forms radium B and C; and that when radium C forms radium D. A fifth is emitted when radium F, or polonium, undergoes further change; the result of this change is unknown. Hence, to take into account the fifth alpha-particle, the total heat must be increased by one-fifth; it then becomes 3.3×10^9 gram-calories. Now, it is possible to calculate, on the kinetic theory of gases, what would be the heat corresponding to the work done by the impacts of the alpha-particles, if their mass and their velocity are known. The velocity of light is 3×10^{10} centimetres per second; that of an alpha-particle is one-fifteenth of that of light, or 2×10^9 centimetres per second; as each atom of radium, of which the atomic weight is 226, sends out five atoms of helium, of atomic weight 4, the weight of the expelled atoms is 20, or about one-tenth of that of the radium. The kinetic energy is equal to that of the sum of the energies of the atoms, or in symbols Sum $\frac{1}{2}mC^2$; substituting figures, we have: $\frac{1}{2} \times 20/226 \times (2 \times 10^9)^2/(42 \times 10^6)$; the last divisor is the heat-equivalent of work, and converts ergs into gram-calories. Simplifying, we have $10/9492 \times 4 \times 10^{18}/10^6 = 4 \times 10^9$ gram-calories. It may be that the velocity of the alpha-particle has been somewhat overestimated, but this number

does not greatly differ from the $3 \cdot 3 \times 10^9$ gram-calories, mentioned above.

It is possible, moreover, to go further, and on the assumption that the motions of molecules may be interpreted as temperature, to calculate the temperature of a space in which alpha-particles are moving with a velocity of 2×10^9 centimetres per second. Now, we have seen on page 91, that the average velocity of a molecule of helium is $1 \cdot 307 \times 10^5$ centimetres per second. Giving the symbol T to the temperature of a helium molecule in the state of an alpha-particle, then, as $(1 \cdot 3 \times 10^5)^2$: $(2 \times 10^9)^2$: : $273 : 6 \cdot 5 \times 10^{10}$ degrees centigrade, or in words, T is sixty-five thousand million degrees. It may of course be objected that what we have been considering is not temperature ; but at all events, it is the equivalent of temperature in the temperature-factor of kinetic energy.

In the third place, we must now consider the known effect of a high temperature on matter. A sketch of " dissociation " was given in Chapter IV ; and it was there shown that exothermic bodies, such as ammonium chloride, dissociate, on rise of temperature, into simpler components. Even elements, like sulphur and iodine, acquire a simpler molecular constitution at high temperatures. Sir Norman Lockyer has, in his book on *Inorganic Evolution*, brought forward incontestable arguments, demonstrating that in the sun and the stars, bodies believed by us, dwellers in a region of

low temperature, to be elementary, split into simpler forms. His arguments may now be shortly summarized.

The evidence is wholly spectroscopic. It begins in 1864, when Mitscherlich pointed out that some bodies known to be chemical compounds when raised to incandescence, give a spectrum special to the compound ; that is, they have a spectrum of their own ; no lines of either of the constituents are seen. Lockyer proved later that when the temperature was high enough to produce decomposition, the lines of the elementary bodies of which the compound was composed made their appearance, according to the temperature employed. Spectra of compounds, at comparatively low temperatures, consist, not of lines, but present a " fluted " appearance, somewhat like the grooves in a Greek column. With rise of temperature, this fluted appearance is replaced by a number of well-defined lines. It was at one time supposed that each element has only one spectrum ; but the opposite is the case ; and the first step is to suggest that in the state of gas the spectrum seen at the lowest available temperature is the spectrum of the molecule of the compound, consisting of two or more atoms ; and that as temperature rises, it is replaced by the spectrum of the atom.

Lockyer points out that as temperature rises, the spectrum of a heated solid grows progressively from the red, through orange, to yellow, green,

blue, and violet ; this is familiar to all, even to those who have never seen a spectroscope ; for we all know that if a poker be heated, it first becomes "red-hot," then yellow, then whiter and whiter, until it is "white-hot." The whiteness is due to the admixture of all the spectral colours, as in ordinary sunlight. He argues that those stars must be the hotter, the farther their spectrum extends towards the ultraviolet.

Next, various plans are open to us to increase temperature ; a flame has a temperature of about 1200°C. ; the electric arc, of about 3500°C. ; a Leiden-jar discharge, a still higher temperature. It is known that as the temperature is successively increased by using the flame, the arc, and the spark, some spectrum lines of many elements become "enhanced," that is, appear more prominently than others ; it is, of course, impossible to get a spectrum at a homogeneously high temperature, because there are all possible lower temperatures, as the vapour escapes out of the hottest region.

In investigating the spectra of the sun and the stars, Lockyer has noticed that the farther the spectrum of the star extends towards the violet end the more such enhanced lines appear ; he therefore concludes that these are signs of higher temperatures than exist in stars with less of a violet spectrum, and fewer enhanced lines.

Taking the metal iron as an example, Lockyer distinguishes four spectra :

" 1. The flame spectrum, consisting of a few lines and flutings only.

" 2. The arc spectrum, consisting, according to Rowland, of 2000 lines or more.

" 3. The spark spectrum, differing from the arc spectrum in the enhancement of some of the short lines and the reduced relative brightness of others.

" 4. A spectrum consisting of a relatively very small number of lines which are intensified in the spark. This we can conceive to be visible alone at the highest temperature in a space efficiently shielded from the action of all the lower ones, since the enhanced lines behave as those of a metal when a compound of a metal is broken up by heat."

Grouping together the enhanced lines of the commoner elements, Lockyer made what he calls a " test spectrum "; and that is practically the spectrum of the sun's chromosphere, the hottest part of the sun; and a star has been examined in which this " test spectrum " exists almost alone, nearly all the lines of which had previously been regarded as " unknown." Iron, for example, has only two lines in the chromosphere, out of two thousand in the spectrum of the body of the sun; and these are precisely the lines which are brightened on passing from the arc to the spark.

On examining the spectra of a series of stars of gradually increasing temperature, as determined by these criteria, all stages in spectra can be followed; and it is remarkable that as temperature

rises the spectra of hydrogen and helium, together
with unknown spectra, appear ; their appearance is
accompanied by the disappearance of the spectrum
of iron, and of other common " elements." And
more ; as the spectra of these elements disappear,
they are replaced by the lines of what Lockyer
terms " proto-elements," which he believes to be
the spectra of elements resulting from the change
of those which we know on this earth ; these in
their turn disappear, to be finally replaced by the
spectra of helium, oxygen, nitrogen, and carbon,
together with some lines which have not been
identified as belonging to any terrestrial element.
Even then, the story is not all told ; for after
helium has disappeared, the spectrum of " proto-
hydrogen " remains ; a spectrum which is numeri-
cally related in wave-length to that of ordinary
hydrogen.

To sum up : " As we come down from the
hottest stars to the cooler ones, the number of
spectral lines increases, and with the number of
lines the number of chemical elements. In the
hottest stars of all we deal with a form of hydrogen
which we do not know anything about here (but
which we suppose to be due to the presence of a
very high temperature), hydrogen as we know it,
the cleveite gases (helium), and magnesium and
calcium in forms which are difficult to get here ;
we think we get them by using the highest
temperatures available in our laboratories. In

the stars of the next lower temperature we find the existence of these substances continued in addition to the introduction of oxygen, nitrogen, and carbon. In the next cooler stars we find silicon added ; in the next we note forms of iron, titanium, copper, and manganese, which we can produce at the very highest temperatures of our laboratories ; and it is only when we come to stars much cooler that we find the ordinary indications of iron, calcium, and manganese and other metals. All these, therefore, seem to be forms produced by the running down of temperature. As certain new forms are introduced at each stage, so certain old forms diasppear."

We have now seen that there are certain elements which are essentially unstable, namely, those which display radioactivity ; that all elements, under the influence of ultraviolet light, emit electrons ; and that in the sun and stars there is undoubted spectroscopic evidence that at enormously high temperatures which reign there a simplification of the elements known to us on the earth has taken place. We have also seen that the amount of energy which escapes during the disintegration of radium and of its products is millions of times greater than escapes during any exothermic chemical reaction, weight for weight ; and that if the kinetic energy of the alpha-particles be translated into the temperature-coefficient of thermal energy, it represents, if we accept the

temperature of the hottest star as 100,000°C. (and this is in all probability an overestimate), 650,000 times that temperature. Can this enormous energy not be utilized, so as to produce transmutation ?

Experiments on these lines have been made, and an account of them will now be given.

The most convenient source of energy is niton. Although, when formed from radium, it has already lost an alpha-particle, still, during its changes to radium D it loses other three ; and that within a month ; for in a month all niton has disintegrated, except a fraction of one per cent. With niton, therefore, we have the great advantage of the expulsion of three alpha-particles in a reasonable time, and all experiments in the direction of transmutation have been made with its help. In all, three series of experiments have been made.

The beginning of the first series was, in a sense, accidental. It was noticed by Giesel that from a solution of a salt of radium, oxygen and hydrogen were continuously evolved ; in a research on this subject an attempt was made to deposit copper from a solution of copper sulphate, instead of producing hydrogen ; it was expected that that metal would be deposited in equivalent amount to the hydrogen. This turned out not to be the case ; a cuprous salt was formed. The copper sulphate used had been re-crystallized several times, and was believed to be pure ; but after it

had been in contact with niton for a month, it was tested for purity, by precipitation with sulphuretted hydrogen, and evaporation of the filtrate. A slight residue was obtained, which showed the spectra of calcium, sodium, and lithium. The presence of the first two was not to be wondered at, for the solution had been kept in glass, a silicate of calcium and sodium. This led to the testing of the copper sulphate for lithium ; and it appeared that commercial copper sulphate does contain traces of lithium.

In the second experiment, copper sulphate, many times re-crystallized, was used ; and before exposure to the niton it was tested for lithium. None was detectable by the spectroscope, after precipitation of the copper as sulphide, in the evaporated filtrate. Specimens of this sulphate were placed in two similar glass bulbs ; one was charged with the niton from about half a gram of radium bromide, collected during a week and sealed ; the other was sealed without any addition. At the end of a month, the contents of each were tested for lithium ; that metal was present in the bulb charged with the niton, but not in the other. This would appear to exclude its having been derived from the glass ; but it might have been extracted from the glass under the influence of the niton ; the glass was therefore tested for lithium, and none was found. With the assistance of Mr. Alexander Cameron, other two experiments of a

similar nature were made ; and also one in which
the bulb was constructed of silica, not of glass.
In all cases lithium was found only in the solution
of copper sulphate which had been treated with
niton ; not in the " blanks." It is only right to
add that Madame Curie carried out a similar
experiment, using a platinum vessel, instead of
one of glass or silica, and obtained no lithium. It
requires considerable practice, however, to detect
very small quantities of matter.

The second series of experiments was also the
consequence of chance. It was required to see
whether a solution of thorium, from which an
emanation proceeds as with radium, yields as the
result of the disintegration of the thorium and its
products, helium. For this purpose, about 400
grams of thorium nitrate dissolved in water was
put into a flask, closed with a tightly fitting stop-
cock ; a little mercury was placed in the flask, so
as to cover the stopcock to the depth of half an
inch, when the flask was inverted. This precaution
was taken to prevent leakage of air into the flask,
which was, to make doubly sure, inverted in a
jar of water, after having been carefully pumped
free from air. As the disintegration of thorium is
much slower than that of radium, a comparatively
large amount of thorium was used, and it was left
for no less a period than six months. On with-
drawing the gas after this time, it was analysed ;
its amount was small ; it contained oxygen,

nitrogen, carbon dioxide, and hydrogen ; it was not certain whether helium could be detected. After six months further keeping, over half a cubic centimetre of carbon dioxide was found, and a possible trace of helium ; a third and a fourth repetition gave similar results. The presence of carbon dioxide was inexplicable ; and a control experiment, in which mercuric nitrate was kept for about the same time, gave only an inappreciable quantity of carbon dioxide. The much more powerful action of niton on thorium nitrate was next investigated ; and four experiments gave, so far as the presence of carbon dioxide is concerned, identical results ; in every case it was found in relatively considerable amount. Experiments were then made with the other elements of the thorium group, namely, silicon as hydrosilici-fluoric acid ; titanium as sulphate ; zirconium as nitrate ; cerium as sulphate ; and lead as nitrate ; also with mercury as nitrate, silver as nitrate, and bismuth as perchlorate. Carbon dioxide was produced under the action of niton from silicon, titanium, zirconium, and a trace from lead and from bismuth ; cerium, silver, and mercury gave no trace of carbon dioxide. Finally, the sample of thorium nitrate which had served for the experiments mentioned was boiled with an oxidizing mixture of potassium dichromate and sulphuric acid ; only a trace of gas could be removed by the pump, and the contraction on treatment with

caustic potash amounted to only a few cubic millimetres ; this proved that the carbon dioxide formed under the influence of niton on thorium had not for its source any carbon compound present as an impurity in the thorium solution. The experiments with silver, mercury, and cerium may be regarded as in a sense " blanks " ; these elements do not appear to yield carbon dioxide.

It had been noticed that when niton was allowed to act on water, not only were oxygen and hydrogen formed in abundance, apparently from the decomposition of the water ; but also that helium and neon were present. Objection was taken to the conclusion drawn from these experiments ; namely, that in presence of water, neon is one of the products of the disintegration of niton. It was stated, and with justice, that it is possible to detect neon in less than 0·5 cubic centimetre of air, if proper precautions be taken. Attention was again directed to this matter, when it was discovered, in course of the analysis of the gases escaping from the King's Well at Bath, that while the argon present in these gases amounted to only three-quarters of that present in an equal volume of air, the volume of the helium was sixty times, and that of the neon one hundred and eighty times as great as those normally present in air. The presence of helium could be accounted for, for the water contains a trace of radium ; and the gases, as much niton in a million litres as would

be in equilibrium with 33 milligrams of metallic radium. Unless, however, water plus niton gives neon, the very large quantity of neon was inexplicable. An experiment was therefore made to measure the neon produced by the action of niton on water; the result may be summarized by the statement that the amount measured would have involved the leakage of no less than four cubic centimetres of air into the apparatus; and so far as was known, there was no leakage whatever. It may therefore be taken as definitely proved that when niton disintegrates in presence of water, neon appears; whether as a disintegration-product of niton, or as the product of the action of niton on water, cannot be determined.

If it is permissible to reason from the analogy of compounds as to the constitution of elements, we know that the higher the molecular weight of a compound, the less stable it is, as a rule; there are, of course, some exceptions. We also know that most compounds are exothermic, that is, they are formed with loss of energy from the elements which they consist of. Analogy would suggest that elements with higher atomic weight should be less stable than those with small atomic weight; and it is noteworthy that uranium and thorium, which of all known elements have the highest atomic weights, are in a state of slow disintegration. Radium comes next in order of high atomic weights, and it is still more unstable; next comes

niton, and, judging from the rate of its disintegration, it is still less stable. Hence the statement with regard to the relative stability of elements must not be interpreted too closely. But it appears legitimate to suppose that elements of medium or of low atomic weight are relatively stable ; and to conjecture that they are exothermic, that is, to cause them to disintegrate, would necessitate an absorption of energy. This is what led to the experiments of which an account has been given. In them the energy of the alpha-particles was utilized.

The beta-particles, however, are also sources of energy ; and it is possible to cause them to act, in the form of " cathode rays," on matter, without having recourse to radioactive substances as their source. It is fairly certain that the energy evolved from radium in the form of beta-rays amounts to not more than 5 per cent of the total ; from one gram of radium it would amount to $1·3 \times 10^8$ calories.

As yet, only a few experiments have been made on the action on matter of beta-rays, which are identical with cathode rays or electrons.

An " X-ray " tube or bulb contains an aluminium cathode, from which, when it is in action, a stream of electrons is projected on to a plate of some resistant metal, from which " X-rays " proceed, apparently by reflection, towards the glass walls of the bulb. These are the rays used to take

" skiographs," or shadow-pictures of the bones of internal organs of the human body. The glass of such " X-ray " bulbs becomes dark purple after prolonged use ; evidently electrons have entered it, and have liberated atoms of sodium (see p. 51). Have they produced any further change ?

To answer that question, the glass of four bulbs which had been long in use was broken up and introduced into a tube of hard glass, placed in a furnace. The tube was pumped empty, and repeatedly washed out with pure oxygen, so as to remove all traces of air adhering to the glass. It was then heated, and the evolved gas was tested for the presence of helium and neon ; both were found, the latter in very minute amount.

An experiment was carried out by Norman Collie, in which precipitated calcium fluoride was bombarded for several days with cathode rays, in presence of a trace of pure oxygen. In order that all adhering gases should be removed, the first four portions of gas pumped off were rejected, and the fifth alone examined. The gas consisted of silicon fluoride, oxygen, and carbon monoxide ; the last was continuously produced. These gases were condensed in cooled charcoal ; and the residue showed the spectrum of *pure neon*, without any admixture of helium. It is premature to speculate as to the source of the neon ; but it is suggestive to note that during its production oxygen was present. The neon was identified

by measurement of nine of its most brilliant lines.

The way is now clear for an exhaustive research on the transmutations of the elements ; for experiment is open to all who can command the means of utilizing powerful cathode discharges.

It appears to me that enough evidence has been accumulated to make it legitimate to speculate on the nature of matter. We know that matter consists of molecules ; " visible molecules " confirm in their behaviour the conclusions drawn from the kinetic theory of gases ; and experiments of the nature of Millikan's and of Wilson's, in the first of which an oil droplet was observed while it was collecting or parting with ions, that is, with electrons associated with matter, and in the second of which the path of a helium molecule through saturated water-vapour was made to reveal its track by the condensation of the steam, appear to me to be an irrefutable proof of the real existence of molecules. That molecules may consist either of single atoms, or of congeries of atoms, is also beyond dispute. That some of the " elements " consist of unstable atoms has also been demonstrated. Let us now consider under what circumstances, and by what means, the elements can be artificially disintegrated, that is, transmuted. And here I wish to acknowledge my indebtedness to Hans Petterson, with whom the question has been repeatedly discussed, and who has put

together the arguments and conclusions in a fashion which I will now reproduce.

It is probable that most of our elements are exothermic ; that is, in order that they shall disintegrate, energy must be conveyed to them ; and judging by analogy with the endothermic elements of the character of radium, it is to be expected that the quantity of such communicated energy must be enormous, if disintegration is to be effected. Moreover, the energy must be in a very " concentrated " form. The most concentrated form of energy we know is that of a helium atom in motion, at a velocity corresponding to a temperature of $6 \cdot 5 \times 10^{10}$°C., or in words, sixty-five thousand million degrees. An encounter may be supposed to take place between such a moving molecule and the atom of some element. What happens at such an encounter ? It is not an ordinary collision, for if it were, after the first few collisions, the particle would have given up by far the greatest part of its kinetic energy to the molecules it met. On the other hand, an alpha-particle from radium C, passing through air at ordinary pressure, follows an almost rectilinear path of 7 centimetres ; and towards the end, when it can no longer be traced on account of its having lost its ionizing powers, it still retains 25 per cent of its original velocity. During its path it can be calculated from the kinetic theory of gases that it has made 450,000 encounters, on the assumption

that the radius of a molecule is 1×10^{-8} centimetre. The only explanation possible is that the alpha-particle passes through the molecules it encounters as a bullet passes through a target.

The passage of the particle through the air produces a very great number of ions in its path. Often it seems to drag an electron with it for a short distance, leaving the molecule which it has passed and robbed positively charged. It may thus be said to have caused a sort of transmutation of the molecule through which it passes ; but as ions are produced, the breakdown is not permanent, for it is reversed when the ions combine. No further effect is produced, and only the very small amount of energy required for the work of ionization is transferred at the encounter, simply because the structure of the atom *as a whole* does not offer sufficient resistance to shocks of this intensity. In short, a reversible change occurs.

Now, supposing the alpha-particle is liberated with its enormous velocity in a solution of a salt already containing ions, it will still have the property of removing with it an electron from an ion which, as its name implies, has already lost or gained one. In the former case, the loss of two electrons may result in an irreversible change ; a transmutation may occur.

The total number of ions produced by an alpha-particle from radium C during its path of 7 centimetres through air at atmospheric pressure is

87,000, out of 450,000 encounters. If the atom be supposed to consist of an outer spherical envelope or shell of the radius given by the kinetic theory of gases, together with a central nucleus of much smaller radius, and probably much greater resistance to impacts ; and if the outer radius of the moving atom of helium—the alpha-particle— be imagined to be of the same magnitude as that of the atom which it encounters, it is easily seen that, out of every four encounters, one will on an average be " semi-central," i.e. the centre of the alpha-particle will pass through the shell of the atom. Now, a quarter of 450,000 is 112,500, a number of the same order as 87,000, the number of collisions attended by ionization.

If, however, the collision is central, what will happen ? Probably 1 in every 8000 collisions is of this central character. The atom struck will be given energy equivalent to a rise of temperature of the order of a thousand million degrees centigrade ; it may be conjectured that in such a case, a sort of ionization of the nucleus of the atom takes place, and it is in the highest degree probable that that would be attended by an irreversible change—in other words by transmutation.

We have now seen what may be termed the evolution of the atom ; the vague speculations of the ancient Greeks ; the bold device imagined by

Dalton to represent the facts of the constant and the multiple proportions in which chemical elements combine with each other ; the introduction of the notion of molecules by Avogadro ; the arrangement of the elements in numerical periods by Newlands, Lothar Meyer, and Mendeléef ; the introduction of the conception of ions by Faraday, and its extension to the state of salts, acids, and bases in dilute solution by Arrhenius and van't Hoff ; the brilliant researches of Perrin, whereby it was proved that visible particles, if sufficiently minute in size, behave in important respects as if they were molecules. We have traced the investigation of electrons, through the early discoveries of Crookes's " radiant matter," to the measurement of their mass and their velocity ; we have followed the remarkable discoveries of the Curies respecting radioactive matter, and the bold generalization of Rutherford and Soddy, who explained the mysterious phenomena by the theory that the bodies displaying radioactivity form a series of unstable chemical elements, each with its own rate of decay. And lastly, arguments have been adduced to show why the belief is tenable that transmutation can be, and has been accomplished, not merely in celestial regions of intense heat, but also by taking advantage of the enormous outpouring of the concentrated energy of niton.

At each stage of the enquiry, theories have been

put forward as to the ultimate nature of matter ; each has been replaced by other theories, somewhat modified from their predecessors, by which a clearer and more consistent idea has been gained of the true nature of things around us. That we shall ever reach finality may be regarded as impossible ; yet the human mind is innately subject to the aspiration of Faust—

"Zwar weiss ich viel, doch möcht' ich alles wissen."

And we know, that although our knowledge is destined never to attain finality, yet, as years roll on, the curve of knowledge will always more and more closely approach the eternal asymptote.

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